Quantitative Assessment of Disinfection By-Products Formed by Chlorine, Chlorine Dioxide and Ozone in Saudi Arabian Drinking Water

BY

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DEDICATION

TO

MY PARENTS

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THESIS ABSTRACT

Name: **Mohammed Al Mutair**

Title: **Quantitative Assessment of Disinfection By-products Formed by Chlorine, Chlorine Dioxide and Ozone in Saudi Arabia Drinking Water**

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This study investigates the effect of different disinfectants on desalinated water blended with raw ground water at different ratios. The study was conducted in three (3) parts namely: chlorination, chlorine dioxide and ozonation. The by-products resulted from these disinfection processes were quantified under different treatment conditions of disinfectant dosage, temperature and reaction time. The correlation between the type of by-products formed and the quality of the source water (desalinated seawater and groundwater) were also investigated in this study. In the first part, the study with chlorine revealed that total Trihalomethanes (TTHMs) formation increases 0 to 247 ppb as chlorine dosages increases from 1 to 5 ppm. The blending ratio of 1:10 (v/v, raw: desalinated) showed the lowest TTHMs formation at chlorine dosage of 1, 2 and 5 ppm. Results showed an increase of TTHMs formation with increasing both reaction time and temperature. In the second part, low chlorite levels resulted from chlorine dioxide disinfection of blended water with mixing ratios of 1:2 and 1:5 was found to increase with dosage of 1 to 5 ppm. But, chlorite species were not detected at blending ratio of 1:10. Finally, in the third part of the study, results showed that bromate formation increased with increase in ozone dosages from 2 to 5 ppm and increase in temperature from 25 to 45^{o}C and reaction time from 5 to 20 min. Significant high levels of bromate were observed in water samples blended with a blending ratio of 1:2, while other blended ratios did not show significant formation of bromate.

ملخص الرسالة

تتناول هذه الدراسة تأثير المعقمات المختلفة على المياه المحلاة المخلوطة مع المياه الجوفية بنسب مختلفة. وقد أجريت الدراسة على ثلاث (3) أنواع من المعقمات وهي: الكلور، ثاني أكسيد الكلور والأوزون. حيث تمت دراسة المواد العضوية والغير العضوية الناتجة بسبب مواد التعقيم المختلفة تحت ظروف مختلفة مثل كمية الخلط، ودرجة الحرارة، وكمية التجريع وزمن التفاعل الكيميائي. كما تم دراسة العلاقة بين نوعية المنتجات العضوية والغير عضوية مع نوعية مصادر المياه (مياه البحر المحلاة والمياه الجوفية). وكشف الدراسة في الجزء الأول أن Trihalomethanes يزيد تركيزه من صفر حتى 247 جزء في البليون مع زيادة جرعات الكلور من 1 حتى 5 جزء في المليون عند ارتفاع درجة الحرارة من 25 درجة مئوية إلى 45 درجة مئوية. وأظهر تركيز THMs أدنى مستوى عند جرعة الكلور من 1 ، 2 و 5 جزء في المليون عند نسبة مزج 1:10 (مياه بحر محلاه/ مياه جوفيه). كما أظهرت النتائج زيادة في تركيز THMs مع زيادة زمن التفاعل ودرجة الحرارة. أما في الجزء الثاني من الدراسة، فإن مستويات منخفضة من الكلورايت نتجت عن التطهير بثاني أكسيد الكلور من المياه المخلوطة مع نسب خلط 1:2 و 1:5 مع زيادة جرعة الحقن من 1 حتى 5 جزء في المليون. ولكن ، لم يتم اكتشاف تركيز من الكلوريت عند نسبة خلط 1:10. وأخيرا في الجزء الثالث من الدراسة ، أظهرت النتائج أن تراكيز عالية من البرومات مع زيادة في جرعات الأوزون من 2 حتى 5 جزء في المليون وزيادة في درجة الحرارة من 25 إلى 45 درجة مئوية وزيادة أيضا في زمن التلامس من 5 حتى 20 دقيقة. ولوحظ ارتفاع مستويات كبيرة من البرومات في عينات من المياه المخلوطة مع نسبة خلط 1:2 ، في حين نسب المخلوطة الأخرى لم تظهر تراكيز كبيرة من البرومات.

CHAPTER 1

INTRODUCTION

1.1 Background

The major source of drinking water in the Kingdom of Saudi Arabia originates from sea water desalination. Saline Water Conversion Corporation (SWCC), the Government Agency responsible for producing desalinated water in the Kingdom, has installed several multistage flash distillation (MSF) and reverse osmosis (RO) desalination plants along the coast of Red Sea and Arabian Gulf. MSF plants contribute the major share of the water being produced in the Kingdom. The distillates from MSF plants are normally blended with adequate amount of groundwater in order to enhance the mineral contents, followed by disinfection before sending to the distributing net works for domestic consumption.

In addition, water is considered as scarce resources in the Kingdom of Saudi Arabia, like many other gulf countries, due to low annual rainfall rates and limited fresh renewable groundwater resources. It is therefore imperative to keep these limited resources free of contaminants and the by-products of their disinfections.

Disinfection of drinking water is an important procedure to control bacterial infection and maintain the water quality. Practically, there are four (4) common disinfectants; chlorine, chloramines, chlorine dioxide and ozone. Almost all desalination plants in the kingdom of Saudi Arabia use chlorine as disinfectant for their product water.

The main concern when using the various disinfectants beside the killing efficiencies of pathogenic germs and the cost is the formation of harmful by- products. These by-products are known of its carcinogenity to the humans and therefore are regulated by the international and national water authorities. While a great wealth of data exits on the DBPs formed in naturally occurring surface and ground water supplies, very little is known on their composition and concentration in desalinated product water. Most of the Saudi drinking water is a blend of desalinated water and raw groundwater. The disinfection processes are usually applied at different stages to ensure the removal of pathogens in the water distribution system.

Disinfection has been used for over a century and has almost eliminated biological water borne disease outbreaks in developed countries (Zwiener, C and S. D. Richardson, 2005). Chlorine was first discovered in 1774 by chemist Karl Scheela (White, G. 1996). It was not until the early 1990's, however, that chlorine was used as a disinfectant (Gordon et al., 1987). Chlorine, ozone, chlorine dioxide and chloramines are the most used disinfectants to minimize the number of pathogens in water. These compounds are strong oxidants and convert natural organic matter to disinfection byproducts (DBPs).

1.2 Formation of DBPs by Different Disinfectants

Chlorine, chloramines, ozone and chlorine dioxide are chemical disinfectants that are used frequently in water treatment to inactivate pathogenic microorganisms, inhibit biofilm formation and oxidize reduced inorganic solutes. Chemical disinfectants are integral to modern water treatment, but not trouble free. Each of the common disinfectants can produce disinfection by-products (DBPs) that pose threats to human

health or aquatic ecosystems. To balance the need for chemical disinfectants with their potential risks, considerable effort has been devoted to understanding the kinetics of formation of DBPs, their toxicity and fate in natural and engineered systems. Disinfection byproducts formation can be summarized by the following:

Disinfectant + Precursor $\longrightarrow$ DBPs

All chemical disinfectants produce organic and/or inorganic DBPs of potential health concern [Table 1]. All disinfectants oxidize naturally occurring organic and inorganic material in water. Disinfectants react with precursors in drinking water to produce DBPs (Phillip C. Singer, 1999). The primary precursor is natural organic matter (NOM) which is generally measured as Total Organic Carbon (TOC) and is comprised roughly 50% carbon, 35% oxygen, 5% hydrogen, 3% nitrogen and lower amounts of phosphorous, sulphur and trace metals. Bromide is also important because it is easily oxidized to aqueous bromine that can also react to form bromine substituted DBPs such as bromoform. DBP formation is affected by various parameters (e.g. PH, Temperature, Disinfectant dose and Residual).

Table 1. Organic and/or inorganic DBPs of potential health concern

Disinfectant	Efficacy as a disinfectant	Provides disinfectant residual in water	Dominant precursors for DBP formation	Dominant DBPs of Regulatory concerns
Ozone	High	No	Bromide & TOC	Bromate (BrO_3^-)
Free chlorine ($HOCl/OCl^-$)	Intermediate	Yes	Bromide & TOC	Trihalomethanes and Haloacetic acids
Chlorine dioxide (ClO_2)	Intermediate	No	Decay of chlorine dioxide	Chlorite and chlorate
Monochloramine (NH_2Cl)	Intermediate	Yes	TOC and organic N	nitrosamines

1.3 Chlorine Disinfection and THMs Formation

In disinfection, gaseous chlorine (Cl_2) is added or liquid hypochlorite (NaOCl) or calcium hypochlorite {$Ca(OCl)_2$} is added to, and reacts with water to form hypochlorous acid. In the presence of bromine hypobromous acid is also formed.

$$Cl_2 + H_2O \longrightarrow HOCl$$

$$HOCl + Br^- \longrightarrow HOBr + Cl^-$$

Hypochlorous and hypobromous acid form strong oxidizing agents in water and react with a wide variety of compounds and destroy efficiently many forms of bacteria and viruses. Hypochlorous acid also reacts with naturally occurring organic matter to form DBPs including four THMs. The two major classes of formed DBPs are THMs and HAAs.

Trihalomethanes (THMs) are small organic compounds similar in structure to methane, but also containing chlorine and/or bromine. The compounds are the major by-products of chlorine disinfection of water supplies. They are formed when naturally occurring organic substances react with chlorine used to disinfect drinking water. The Trihalomethanes of significance in disinfected water are chloroform, dichlorobromomethane, chlorodibromomethane, and bromoform.

The structure of halomethanes is based on methane. Halogen takes up the binding places of hydrogen atom. At the center of each of the four {trichloromethane, ($CHCl_3$), tribromomethane ($CHBr_3$), bromodichloromethane (BDCM, $CHCl_2Br$) and dibromochloromethane (DBCM, $CHClBr_2$) is a carbon atom and it is surrounded by and bound to four atoms: one hydrogen and three halogens. These four compounds are collectively termed Trihalomethanes and abbreviated as either THM or TTHM (total trihalomethanes).

Especially chloroform, bromoform and BDCM are human hazard (Eva Agus, et al., 2007). An important influence of THM formation is hydrophobic organic matter (contains more aromatic compounds). More THMs are produced if in the organic matter is more Halogen hydrophobic than hydrophilic matter (Liang, L and P.C. Singer, 2003).

The first DBPs were discovered in 1974. Studies showed that when hypochlorous acid react with naturally organic matter in water form many disinfection by-products including THMs (Rook, J. J, 1974). The discoveries of THMs in drinking water lead to research on other chemicals formed when chlorine is added, and to the health effects of these chemicals. Typically, there exits two sources of water for drinking water production,

namely, surface water and ground water. Ground water is usually better quality as compared to surface water. Surface water contains higher levels of organic matter and particles. Therefore higher amounts of disinfectants combined with higher organic matter and other compounds in the surface water usually lead to more DBPs than disinfection of ground water (Krasner, S. W., et al., 2006).

The WHO International Agency for Research on Cancer (IARC) reviews research conducted on potential carcinogens and has classified possible human carcinogens [Table 2]. To develop the guideline values for drinking water, WHO reviewed the literature and documented studies (WHO, 1996) showing health effects from exposure to each THMs. The WHO guideline values (WHO, 1993) for THMs are shown in Table 3. The USEPA does not regulate THMs or Halo acetic Acids (HAAs) individually (USEPA, 2003), there is only a standard for total THMs and total HAAs [Table 4].

Table 2: IARC Classification of THMs Carcinogenicity

DBP	Humans	Classification
Chloroform	Inadequate evidence for human carcinogenicity	Possible human carcinogen (Group 2B)
Bromodichloromethane	Inadequate evidence for human carcinogenicity	Possible human carcinogen (Group 2B)
Dibromochloromethane	Inadequate evidence for human carcinogenicity	Not classifiable as to its carcinogenicity in humans (Group 3)
Bromoform	Inadequate evidence for human carcinogenicity	Not classifiable as to its carcinogenicity in humans (Group 3)

Table 3: WHO Guideline Values for THMs in Drinking Water (WHO, 1996)

DBP	WHO Guideline Value
Chloroform	200µg/l
Bromodichloromethane	60µg/l
Dibromochloromethane	100µg/l
Bromoform	100µg/l

Table 4: D/DBP Rule Implementation, USEPA

Stage	TTHM Standard	HAA Standard
Initial	100 µg/L	
Stage 1	80 µg/L	60 µg/L
Stage 2	40 µg/L	30 µg/L

Most of the desalination plants produce their own chlorinating agent by electrolysis of seawater to generate chlorine, which is allowed to react with co-generated sodium hydroxide to form sodium hypochlorite. This seawater generated sodium hypochlorite (NaOCl), is dosed to product water in the form of crude chlorinating agent contained in the parent seawater matrix. Thus there has been increasing concern on the occurrence of numerous disinfection byproducts (DBPs) which may contaminate product water. Some of these DBPs {Trihalomethanes (THMs) & Haloacetic acids (HAAs)} are known to have toxic effects on human health if administered in small amounts, while the toxicity of a great majority of them is still unknown. Especially the brominated DBPs can lead

to serious health problems, often they induce cancer. Bromate is one of these toxic DBPs formed by Ozonation of bromide in water.

Health Effects of THMs

The health effects of THMs are unclear. Studies of human populations have indicated a slightly higher incidence of bladder and colon cancer in areas where the drinking water has been chlorinated. Other studies, however, have not shown an increased risk of cancer. While animal studies have shown mutagenic and carcinogenic potential of THMs, it has been suggested that these results are unreliable since the animals are exposed to THM levels 10,000 times greater than humans are exposed to.

Some epidemiological studies have found associations between adverse reproductive outcomes and consumption of drinking water high in THMs, and some have not detected the associations. Studies continue to be conducted to better define whether there is a link between consumption of drinking water high in THMs and the risk of low birth weight or other adverse effects on pregnancy.

Are the Levels of Trihalomethanes in Drinking Water Dangerous to Health? Several epidemiological studies have suggested a weak association between exposure to chlorinated surface water and certain cancers, and reproductive and developmental effects. Because of the large population exposed to chlorinated drinking water, the health risks associated with THMs, even if small, need to be taken seriously. For this reason the limit for THMs was reduced from100 µg/l to 80 µg/l (under the Stage 1 disinfectant and disinfection By-Products Rule). By converting from chlorine to chloramines disinfection

in early 2004, the SFPUC reduced total THMs to < 30 µg/l, well below the Environmental Protection Agency's standard for drinking water.

These trihalomethanes have been linked to induction of tumors in target organs (e.g., liver, kidney and bladder) of experimental animals (J.C. Coffin, et al, 2000). Human epidemiological studies also have correlated increased levels of brominated trihalomethanes in drinking water with increased colorectal and bladder cancer incidence and mortality (C.Y. Yang, et al, 1998). Trihalomethanes also have been shown to act as reproductive and developmental toxicants in several laboratory studies and have been linked to adverse reproductive effects in one epidemiological study (K. Waller, et al 1998 and F. Bove, et al, 2002).

1.4 Chlorine Dioxide (ClO_2) and Chlorite Formation

Chlorine dioxide is an attractive alternative to chlorine in drinking water disinfection because it effectively inactivates bacteria and virus over a broad pH range, does not produces THMs, controls taste and odor compounds, oxidizes iron and manganese provides measurable (Nancy Gonce and Evangelos A. Voudrias, 1994; Werdehoff K. S. and Singer P. C. 1987). In water treatment practice, most common of the ClO_2 reactions with substances in water are in a mildly acidic, neutral or mildly alkaline environment and results in its reduction to the chlorite ion (ClO_2^-) (Miller G. W. et al., 1978). At alkaline pH values, chlorine dioxide undergoes a disproportionation reaction to produce ClO_2^- and chlorate (ClO_3^-) ions (Gordon G. et al., 1972).

The major disadvantage of chlorine dioxide is the formation of potentially harmful inorganic byproducts, chlorate and chlorite ions (Couri D. et al., 1982). It has been reported that ClO_2, ClO_2^- and ClO_3^- will cause hemolytic anemia with the greatest effect shown by chlorite ion on rats and mice through drinking water. The USEPA currently recommends that the combined residuals of ClO_2, ClO_2^- and ClO_3^- not exceed 1mg/l in the distribution system (Gordon G. et al., 1990; Pontius F. W., 1990). Other reaction by-products of chlorine dioxide with organics in drinking water have not been well characterized but include aldehydes, carboxylic acids, haloacid, chlorophenols, quinines and benzoquinone (Bull R.J. and Kopfler F. C., 1991). In a recent article, more than 40 organic disinfection by-products were identified in a pilot plant in Indiana, which uses chlorine dioxide as a primary disinfectant. The toxicity of these by-products is largely unknown (Larson R. A and Weber E. J., 1994).

Health Effects of Chlorite

Exposures to chlorate and chlorite have both been shown to have adverse effects on the blood. Chlorate has additional health effects including abdominal pain, diarrhea, coma, and at high enough levels, will cause death. Further research needs to be conducted to determine the mutagenic and carcinogenic potential of chlorate and chlorite.

Chlorine dioxide is rapidly absorbed from the gastrointestinal tract. No particular organ appears to selectively concentrate the dose following exposure (Abdel-Rahman MS, 1985). The toxicity of chlorine dioxide, chlorite and chlorate is considered to be the same because chlorine dioxide and chlorate can be rapidly converted to chlorite in the human body [Lyman, W. C., 1986).

1.5 Ozonation (O_3) and Bromate Formation

Ozonation is a powerful oxidizing treatment of water. It kills many forms of bacteria's and parasites which are resistant to conventional disinfectants (chlorination, ClO_2, etc.). Ozonation minimizes the formation halo organic DBPs like THMs and HAAs. Ozone reacts most with double bonds, activated aromatic systems and non-protonated amines (Von Gunten U., 2003). High concentration of bromide (Br^-) in the range of 50 to 100µg/l is most problematic, because it leads to the formation of bromate (BrO_3^-). Bromate is fixed as a class 2B carcinogen by the international agency of research in cancer (IARC); it means that bromate is possibly carcinogens for human.

What is bromate? Bromate is a chemical compound containing bromine. It is a by-product of disinfection mostly associated with ozonation of bromide-containing waters. Bromate (BrO3) is an oxyanion of bromine which can be found in potable drinking water. It is a by-product mostly generated when raw water sources (both surface and ground waters) containing bromide ions are treated with ozone. It is also formed in water following pretreatment processes including hypochlorination, where it is a contaminant of hypochlorite feed stocks.

Bromate formation during the oxidative treatment of bromide-containing water has been of great concern ever since bromate was classified as carcinogen. Saudi Arabia groundwater is coincidentally high in bromide content and the potential of forming bromate during the treatment of such water is high.

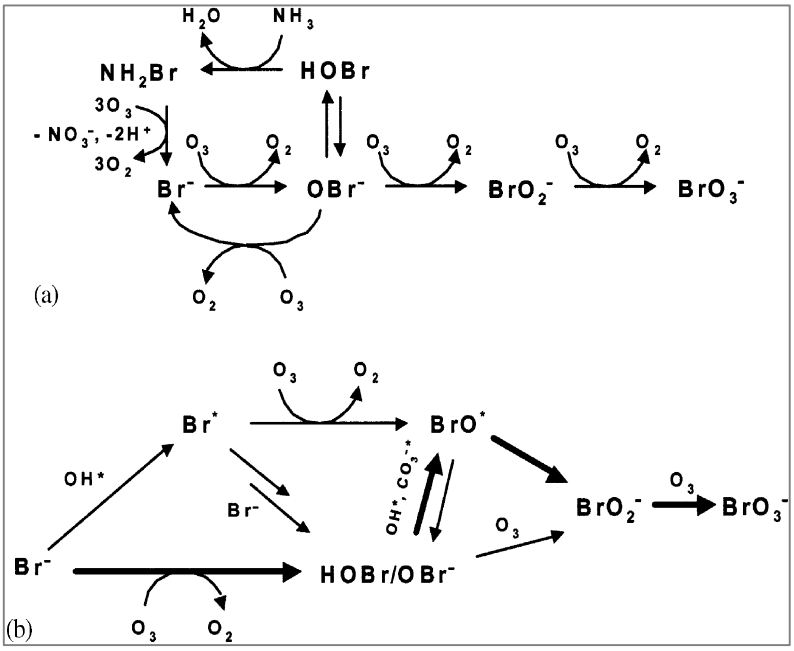

Figure 1. Reaction scheme for bromate formation during ozonation of bromide-containing waters. (a) Reactions with ozone and (b) reactions with ozone and 0H radicals. The bold lines show the main pathway during the secondary phase of an ozonation process. Adapted from (Von Gunten U., 2003).

Two different possible ways for the formation of bromate has been proposed (Von Gunten U., 2003). The first one includes an oxidation of bromide (Br^-) by ozone (Fig. 1a), the second one is a reaction with ozone and OH radicals (Fig. 1b). Both processes include up to six oxidation states of bromide. In water, both reactions run simultaneously. The first reaction (Fig. 1a) starts with an oxidation of bromide (Br^-) by ozone. An oxygen atom binds to bromide and produces hypobromite (OBr^-). Ozone oxidizes OBr^- to BrO_2^- and following BrO_2^- to BrO_3^- (bromate). The free Br^- ion can also form at the start of the reaction by ozonation. The second possible reaction (Fig. 1b) occurs by transfer of Br^- to Br radicals (Br^+) by OH radicals (OH^+). Br^+ decay to $HOBr/OBr^-$ or can be oxidized by ozone to BrO radicals (BrO^+). The BrO^+ decays to

BrO_2. The next step is an oxidation with ozone to bromate. $HOBr/OBr^-$ undergoes two oxidations with bromate as product or will be transferred with OH^+ to BrO^+.

Health Effects of Bromate

While bromide ion is mostly not considered to be harmful in the concentrations found in drinking water, bromate pose serious health concerns. Information on the toxicity of bromate comes from accidental or international poisonings in people and form studies on laboratory animals.

Bromate poisoning causes abdominal pains, hearing impairment, kidney failure and at high enough doses, may cause death. Animal studies have also shown that bromate is mutagenic and carcinogenic to the kidneys in particular. Long term exposure to high levels of bromate has also caused cancer in laboratory animals. Whether bromate can cause cancer in people is not certain, but the World Health Organization (WHO, 1993) and the international Agency for Research on Cancer (IARC) classified Bromate as group 2B or a 'potential human' carcinogen (WHO, 1993). It was due these facts that the control and regulation of bromate in drinking water became essential.

In addition, the USEPA in first stage Disinfectant and disinfection by-products Rule has recommended a maximum contaminant level goal (MCLG) of zero for bromate.

Recently, Saudi Arabian Standards Organization (SASO) set a new drinking water standard regulation related to bromate concentration which was lowered from 25 ppb to 10 ppb (Standard No.409/2000).

CHAPTER 2

LITERATURE REVIEW

Chemical disinfectants are used in desalination plants for pre-treatment and for disinfection of water after desalination. They are applied during pre-treatment to control bio-fouling on intake structures, to improve the performance of filters and to control bio-fouling on membranes. In desalination plants using disinfectants, many of the DBPs formed during pre-treatment will be discharged in the brine where they could affect aquatic ecosystems if they are not diluted sufficiently after discharge. Disinfectants also are applied prior to sending the water into the distribution system. In some cases, DBPs may be formed when desalinated water is blended with water from other sources prior to disinfection or when desalinated water and water from other sources mix in the presence of a residual disinfectant in the distribution system. In most existing desalination plants, free chlorine (i.e., $HOCl/OCl^-$) is used for pre-treatment and final disinfection and most of the available data from desalination systems pertain to chlorine DBPs.

2.1 Studies on Trihalomethanes Formation Due to Chlorination

The kinetics of DBP formation and the nature of DBPs formed are affected by the presence of bromide and iodide. For example, elevated concentrations of bromide lead to enhanced production of brominated DBPs during chlorination (S.W. Krasner, et. al.1996) and enhanced bromate production during ozonation (W.R. Haag and J. Hoigne, 1983). Brominated and iodinated DBPs are particularly problematic because they often are more

carcinogenic or mutagenic than their chlorinated analogs (S.D. Richardson, et al. 2003 and M.J. Plewa and E.D. Wagner, 2004). As a result, much of the current research on drinking water DBPs isfocused on newly discovered brominated and iodinated DBPs. The concentrations of bromide in surface and ground waters normally reflects the composition of seawater because the ion often originates directly from marine sources (e.g., seawater intrusions into coastal aquifers) or is derived from salts formed during the evaporation of seawater (e.g., halide applied to roads during winter). As a result, the highest concentrations of bromide are usually detected in arid regions with high rates of evaporation, such as the Mediterranean, southwestern Australia and the Western United States. In such arid regions, concentrations of bromide in freshwater sources can be up to an order of magnitude higher than the median concentrations detected in a survey of US water supplies.

A study conducted by (P. C. Mayanakutty, et al., 1989) for monitoring the organic compounds in desalinated water samples in Al-Jubail, Al-Khobar, and Al-Khafji desalination plants did not indicate the presence of any toxic chemicals in significant concentrations. However, high concentrations of several organics were detected in hypochlorite samples produced by sea water electrolysis, but most of them were below detection levels in chlorinated sea water used as make-up in the desalination plants. This may be due to either high dilution with un-chlorinated sea water or transient nature of most of these compounds. Although some organics were detected in make-up sea water, almost all of them were rejected during the distillation process.

Effect of pH on the formation of THMs was found to increase with increase in the pH from 6 – 8 (Liang, L. and P. C. Singer, 2003). It was also observed that in warmer water more THMs are produced than in colder (Richardson, S. D. et al., 2003). Formation of bromoform and dichloromethane has been found in disinfected water containing bromide. Dissolved organic carbon has also been found to effect the formation of brominated THMs. A high concentration of brominated THMs is observed at low organic carbon concentration (Richardson, S. D. et al., 2003).

In their study, (Tawabini, et al., 1987) showed that there was an increase in the formation of THMs with increase in chlorine dosage in distilled water (obtained from synthetic seawater) blended with ground water. Chlorine frequently is applied for disinfection after desalination at typical concentrations of approximately 1 mg/l as Cl_2. Depending upon the length of the distribution system, the chlorine contact time can be as long as several days (F.S. Al-saleh and A.S. Al-haddad, 1994 and M. Hafsi, et al. 2004). Given the relatively low dose of chlorine applied at the treatment plant, DBP precursors that pass through desalination systems may be converted to DBPs within the distribution system rather than in the desalination plant. The term trihalomethanes typically refers to chloroform ($CHCl_3$), bromoform ($CHBr_3$), iodoform (CHI_3) and all of the species with mixed halogens (e.g., dichlorobromomethane — $CHCl_2Br$). Concerns associated with trihalomethanes in drinking water began after reports of the production of chloroform in chlorine disinfected water (J.J. Rook, 1974 and T.A. Bellar and J.J. Lichtenberg, 1974).

Following the discovery of chloroform in chlorinated water, scientists reported the formation of brominated trihalomethanes (J.J. Rook, 1974 and S.W. Krasner, et al. 1989

and W.J. Cooper, et al 1985). Recently, iodinated trihalomethanes also have been detected in chlorinated waters (Y. Bichsel and U. von Gunten, 2000 and G.H. Huaand J. Kim, 2006) at much lower concentrations than the chlorinated and brominated trihalomethanes. Chloroform, bromodichloromethane and bromoform are classified as probable human carcinogens by the United States Environmental Protection Agency (USEPA) (USEPA, IRIS database, 2007). Numerous studies have demonstrated a shift in the speciation of trihalomethanes produced during chlorination from predominantly chloroform at low bromide concentrations to bromoform at high bromide concentrations (T.V. Luong, et al, 1982). The shift in trihalomethane speciation is important because the brominated compounds tend to be more toxic than their chlorinated analogs (M.G. Muellner, et al, 2007 and S.D. Richardson, et al, 1999). The formation of brominated disinfection by-products is attributable to the conversion of hypochlorous acid to hypobromous acid, which occurs through an acid-catalyzed reaction (K. Kumar and D.W. Margerum, 1987) with the net stoichiometry:

$$HOCl + Br^- \rightarrow HOBr + Cl$$

The relationship between Trihalomethanes speciation and bromide concentration is complicated by variations in concentrations of Trihalomethanes precursors, which normally are correlated with dissolved organic carbon concentrations. The speciation of Trihalomethanes also is affected by the ratio of hypochlorous acid to bromide because bromide is depleted at high chlorine doses. In general, a higher degree of bromide substitution into the Trihalomethanes is observed at low dissolved organic carbon concentrations because the bromide is depleted during the reactions (A. Obolensky and

P.C. Singer, 2005). The presence of bromide also results in an increase in the total concentration of Trihalomethanes formed on a molar basis, with total Trihalomethanes concentrations nearly doubling as bromide concentrations increase from <70 µg/l to approximately 2,000 µg/l (G.H. Hua, et al, 2006). The higher yield of Trihalomethanes in the presence of bromide is attributable to the tendency of HOBr to undergo substitution reactions more readily than HOCl G.A. Cowman and P.C. Singer, 1996). Blends of desalinated water and water from other sources can result in the production of more Trihalomethanes than would be predicted by taking a weighted average of the concentrations of Trihalomethanes produced in the waters prior to blending. For example, chlorination of a mixture of equal volumes of surface water and desalinated water resulted in the formation of 0.30 µM of trihalomethanes (54 µg/l) compared to a predicted value of 0.23 µM obtained by averaging the concentrations of Trihalomethanes formed when the surface water and the desalinated water were chlorinated separately (McGuire Consultants, 2004). Bromoform will be the predominant THM formed when chlorine is used for seawater pretreatment or disinfection of desalinated water.

(A. M. Shams El Din, et al., 1991) investigated the contribution to the problem of Trihalomethanes (THMs) formation from the Arabian Gulf Water. They found that chlorinated clean seawater contain bromoform (BF), di-bromochloromethane (DBCM), di-chlorobromomethane (DCBM) and chloroform (CF). They found that bromoform make 95% of the THMs.

(Al-Mudhaf et al., 2009) investigated the household drinking water samples. This water was from desalination plants along Kuwait's coast. This distilled water was then blended

with 5–10% brackish water to make it potable. Finally, this water was chlorinated and pumped to a house hold distribution network. In addition to the four THMs species that were previously reported in detail, between one and six of the nine compounds DBM, 1,2-DCP, toluene, 1,2,4 TCB, naphthalene, 1,2,3-TCB, total xylenes, benzene and 1,2DBCP were found in household water with detection frequencies ranging from 0.2% for 1,2-DBCP to 91.3% for DBM.

A comparative study (T. S. Imo, et al., 2007) of Trihalomethanes was carried out in the drinking waters of Okinawa islands, Japan, wherein both ozonation and chlorination was used as primary and secondary disinfection. They found that brominated compounds were more common in all the samples. The Trihalomethanes levels were well below the guidelines values in Japan but in some samples it was found to exceed the WHO values. They found that the mean concentration of Trihalomethanes from treatment plants in Okinawa ranged from 0.30 ± 1.81µg/l to 11 ± 2.68µg/l and from the consumption sites ranged from 2.08 ± 0.32 µg/l to 19.39 ± 100 µg/l.

2.2 Studies on Chlorite Formation Due to Chlorine Dioxide

The influence of reaction time, concentration of chlorine dioxide dosed, pH, temperature, UV irradiation on the formation rates of Chlorate and chlorite in the water treatment using chlorine dioxide was studied by Yoon-jin Lee. (Yoon-jin Lee, et. al., 2004).

When the initial concentrations of chlorine dioxide were 0.5, 1 and 3mg/l, the concentrations of chlorine dioxide remaining were 0.01, 0.16 and 1.89mg/l after 120min. The ratios of residual chlorine dioxide to initial chlorine dioxide were 2.0, 16.3 and

63.1%. The concentration of chlorite formed was shown to increase more rapidly when chlorine dioxide was dosed in high concentration, but the transformation rate decreased more slowly. The concentration of chlorate formed was also shown to be higher when the initial concentration of chlorine dioxide was higher. However, when chlorine dioxide was 0.5 mg/l, chlorate was not found. But when chlorine dioxide was 1 and 3mg/L, the ratios of chlorate transformed from chlorine dioxide were 1.0 and 14.9%. To not exceed the MCLs (Maximum contaminant levels) for chlorine dioxide and chlorite recommended by USEPA, it appeared that chlorine dioxide dose should not exceed 1.64 mg/l in the case of this sample (DOC=2.91 mg/l).

In alkaline solution, as the conversion ratio to by-products was higher, chlorine dioxide was decomposed relatively faster. Especially when pH was 10, chlorine dioxide reacted with the reductants in water continuously and was converted to by-products most greatly compared to other pH range. This may have been caused by the disproportionate reaction of chlorine dioxide under basic conditions:

$$2ClO_2+2OH \rightarrow ClO_2 + ClO_3 + H_2O$$

On the other hand, the concentration of chlorate formed was higher when pH was lower. At pH 7, chlorate was transformed to about 10% from chlorine dioxide. Meanwhile at pH 4, chlorate was transformed to about 15% from chlorine dioxide. By the way, at pH 10, chlorate was not formed at all. In condition of low pH, chlorine dioxide converts to chlorate as shown by (Rav-Acha et al., 1984).

$$4ClO_2+4H^+ + 4e \rightarrow 4HClO_2$$

$$4HClO_2 \rightarrow 2ClO_2+ClO_3^- + Cl^- +2H^+ + H_2O$$

As temperature affects the rate of reaction, chlorine dioxide consumption increased with temperature. The ratios of chlorine dioxide consumed to chlorine dioxide dosed were 77.2, 83.7 and 98.6% after 120 min at 10, 20 and 30^{o}C. The formation of chlorite was considerably active at lower temperature. The percentage of chlorite transformed from chlorine dioxide was 59.0 and 60.5% at 10 and 20^{o}C, respectively, but it reached even 80.2% at 30^{o}C.

Concentrations from below 2 to 420 mg/l for chlorite were first reported in hypochlorite solutions by Bolyard et al. (1992), (Bolyard M, et al., 1992) but not at measurable levels in drinking water. One year later, the same authors (Bolyard et al., 1993) reported to have found chlorite only when disinfecting with chlorine dioxide, but chlorate (21–660 µg/l) when disinfecting either with chlorine dioxide or hypochlorite, in comparable concentrations. Thus, in the water industry, chlorate is considered to come from the hypochlorite reagents, while chlorite is from the treatment with chlorine dioxide. Regarding the calcium hypochlorite pellets, contents of chlorite (median 695 mg/kg) and chlorate (median 9516 mg/kg) were found to be much lower than those of the sodium hypochlorite solutions (Rafael J. Garcia-Villanova, et al., 2010).

The inorganic species, chlorite (ClO_2^-) and chlorate (ClO_3^-) are the major by-products of chlorine dioxide disinfection in drinking water treatment plants. The production of chlorite and chlorate vary depending on the source NOM in the raw water. Typically, up to 60% of the applied ClO_2 dose is reduced into chlorite ion and up to 10% is converted into chlorate ion (C. Collivignarelli and S. Sorlini, 2004). As a result of the lower reactivity of ClO_2 with organic matter, formation of the regulated THMs and other

haloorganic by-products is not observed from use of this disinfectant (J.W. Li, et al, 1996, G. Svecevicius, et al, 2005 and A.A. Stevens, 1982). In the absence of bromide, chlorine dioxide, DBPs typically include oxygen-containing organic compounds (e.g., aldehydes, ketones, maleic anhydrides, and carboxylic acids (W.G. Miller, et al, 1978 and S.D. Richardson, et al, 1994). At bromide concentrations comparable to seawater and desalination product water, formation of brominated organic by-products has been observed in a laboratory study, although in a kinetics study, ClO_2^- and ClO_3^- did not react with bromide ion to form HOBr, the reactive species with dissolved aquatic organic matter (J. Hoigne and H. Bader, 1994). In humic acid solutions containing 5 mg/l of Br, bromoform was the only trihalomethane detected after chlorine dioxide disinfection (J.W. Li, 1996). The use of ClO_2 in combination with chloramines on high-bromide water, however, has been shown to enhance the formation of brominated trihalomethanes and cyanogen bromide (CNBr) in amounts exceeding the sum that would have formed from the individual disinfectants (Grossman,1999).

2.3 Studies on Bromate Formation Due to Ozonation

Until the extensive application of ozone as an oxidant–disinfectant for the treatment of drinking waters during the last decades, no concern had risen regarding the presence of bromate in them. The bromide ions in frequently present in some source waters are oxidized to bromate by ozone, so that regulations in some countries, like Spain, only consider its analysis for the case of this treatment. A comprehensive body of scientific literature has been produced on this topic, so that the problem seemed to remain restricted to the ozonation process. In the year 1992 it was reported that bromate ions were also

present in the sodium hypochlorite solutions historically employed as a disinfectant reagent for many drinking waters. Amounts of 4 to 51mg/l were found in hypochlorite feedstock solutions (Bolyard et al., 1992).

In terms of by-product formation, ozonation typically minimizes the formation of conventional haloorganic DBPs like Trihalomethanes and haloacetic acids. Although halogenated organics are not formed at significant concentrations fromozonation of NOM, they are produced when subsequent chlorination and chloramination follows ozonation (I. Najm and R.R. Trussell, 2001). Ozonation of high-bromide waters, such as found in desalination systems, can produce BrO_3 at concentrations of one to two orders of magnitude above its regulatory standard. After ozonation of waters with high bromide levels, oxidation by O_3 and OH radicals occurs in a complex reaction scheme which involves up to six oxidation states of bromine (A.T. Koga and W.H. Glaze, 1991 and L.B. Richardson, 1981). The major inorganic by products of these reactions in aqueous systems include BrO_3, hypobromous acid/hypobromite ion (HOBr/OBr) and hydrogen peroxide (H_2O_2). HOBr/OBr^- and H_2O_2 are generally unstable and may act as a residual disinfectant. Ozonation of raw water containing as low as 50 µg/l of bromide produces bromate at concentrations in excess of the regulatory threshold (R. Butler, 2005 and U. von Gunten and U. Pinkernell, 2000). Optimization of plant ozonation conditions may control bromate formation for source waters containing up to 150 µg/l Br^- (U. von Gunten and U. Pinkernell, 2000). One strategy involves addition of ammonia as a sink for HOBr, a vital intermediate in bromate formation. Another strategy is lowering the pH to favor HOBr and suppress the oxidation of the dissociated hypobromite ion (OBr^-).

Ozonation, even with these control steps, is still unsuitable for use in bromide-rich waters in desalination systems. At the level needed for microbial inactivation, ozonation of coastal groundwater affected by seawater intrusions (typical bromide concentrations of 4 mg/l) produced ~300 µg/l BrO_3 (T. Myllykangas, 2000). Increased temperature has been shown to increase the rate of bromate formation as a result of increased reaction kinetics and because the equilibrium between $HBrO_3 \rightarrow BrO_3^- + H^+$ shifts to the right as the temperature increases due to a commensurate increase in the acidity constant (Legube et., al 2004).

The dose rate of ozone has a significant effect on the formation of bromate (Wert E. C., et al., 2007) and was shown to have a linear relationship. Lowering of pH was found to minimize the bromate concentration (Bull R. J and Kopfler F. C., 1991).

In summary, the thorough literature survey conducted at this stage revealed that little has been done on assessing the formation potential of various DBPs when blended water is disinfected with chlorine, chlorine dioxide and ozone.

CHAPTER 3

RESEARCH OBJECTIVES

The main objectives of the study is to identify and determine the levels of bromate, chlorite and THMs by-products in a blended water by using different disinfectants. The specific objectives of the study include:

1. Study the effect of source water quality on the formation of by-products.
2. Study the effect of blending ratios on the levels of disinfection by-products.
3. Determine the optimum disinfection condition to achieve the minimum DBP.

CHAPTER 4

MATERIALS AND METHODS

4.1 Preparation of Blended Water Sample

4.1.1 Desalinated Water Samples

Desalinated (product water) samples were brought from Al-Jubail desalination plant produced by MSF. The plant treats seawater from the coast of the Arabian Gulf. The most common method of seawater desalination in the Arabian Gulf area is thermal seawater desalination. In this method seawater is pre treated with biocide to kill micro organism present in the seawater. The seawater entering the evaporator is further treated with anti scale chemicals to prevent scale formation in the evaporator heat exchange condenser tubes .The treated water is then heated in brine heater of distiller plant called evaporator, to a pre determined temperature normally between 108^{o} to 112^{o}C. The heated water is then passed through a series of chambers which are maintained under vacuum. The heated seawater flashes due to vacuum. The vapor thus released is condensed by the circulating brine at lower temperature. Thus distillate is produced in each of the flash chamber stages. The distillate from each stage is collected in the last stage of the evaporator. The distillate thus produced has slightly corrosive properties as the produced distillate pH is 6.8 - 7.2.

4.1.2 Raw Brackish water samples

Raw brackish groundwater samples were obtained from local wells extracted from a depth of 140 m. The well is feeded from Al-khober aquifer of Dammam formation.

4.1.3 Characterization of Water Samples

Water samples used were analyzed and their compositions are shown in Table 5.

4.1.4 Blending of Water Samples

Desalinated water samples were collected from the Jubail Plant and were blended with ground water in certain ratios as shown in the Table 6.

4.2 Standards and Reagents

4.2.1 De-ionized Water

De-ionized waters were used throughout the experiment. The water freshly de-ionized from the Milli-Q Deionizer and stored in clean glass containers.

4.2.2 Ultra Pure Water

Ultra pure water was obtained by passing deinonized water through Pure Lab Ultra unit from Elga Company.

4.2.3 Standard Potassium Bromate ($KBrO_3$) (1000 ppm)

Standard solution of Potassium Bromate from (BDH) containing 1000 ppm of bromate was prepared by dissolving 1.3057 g of AR grade Potassium Bromate in one liter of ultra

pure water. Standard solutions of lower concentrations were freshly prepared from this stock solution as required.

Table 5. Quality of distillate (product) and well water samples

Parameters	**Unit**	**Distillate water**	**Well water**
PH		6.5	7.20
Conductivity	µS/cm	20	3600
TDS	mg/l	12	1700
M-Alkalinity	mg/l	5	140
Chloride	mg/l	6	880
Sulfate	mg/l	< 1	660
Bromide	mg/l	0.014	1.2
Calcium	mg/l	< 1	187
Magnesium	mg/l	< 1	88
Potassium	mg/l	< 1	3
Sodium	mg/l	2	459

Where the well water from Khober aquifer of Dammam formation (140m)

Table 6. Quality of blended water samples

Parameters	**Unit**	**Blended water (R)**		
		1:2 v/v	**1:5 v/v**	**1:10 v/v**
PH		7.1	7.0	6.9
Conductivity	µS/cm	1000	500	230
TDS	mg/l	680	435	208
M-Alkalinity	mg/l	6.0	10.0	15
Chloride	mg/l	85	68	32
Sulfate	mg/l	20	16	12
Bromide	mg/l	0.98	0.50	0.25
Calcium	mg/l	40	28	18
Magnesium	mg/l	4	3	2
Potassium	mg/l	<1	<1	< 1
Sodium	mg/l	56	40	16
TOC	mg/l	0.098	0.075	0.056

Where R= X:Y

X= Volume of raw brackish water

Y= Volume of distillate (product) water

4.2.4 Sodium Chlorite Standard Solution (1000 ppm)

Standard solution of Sodium Chlorite (31.5%) containing 1000 ppm of chlorite was prepared by dissolving 3.2 ml in one liter of ultra pure water. Standard solutions of lower concentrations were freshly prepared from this stock solution as required.

4.2.5 THMs Stock Standard Solutions

THMs stock standard (1000 ppm) was obtained commercially from Supelco Co. was used in this study. Standard solutions of lower concentrations were freshly prepared from this stock solution as required.

4.2.6 Sodium Sulphite (Na_2SO_3)

Sodium Sulphite (95%) manufactured by BDH chemicals Ltd was used to quench ozone, chlorine and chlorine dioxide reaction in the treated water.

4.2.7 Calcium hypochlorite (1000 ppm)

1.6092 g of $Ca(OCl)_2$ (70% NIPPON SODA CO., LTD, JAPAN) was prepared by diluting to1000 ml of ultra pure water in a standard volumetric flask. Standard solutions of lower concentrations were freshly prepared from this stock solution as required.

4.2.8 Concentrated Hydrochloric Acid Solution

Concentrated HCl (36%) was used for the preparation of Chlorine Dioxide solution and obtained commercially from Fisher Chemicals, NJ, U.S.A.

4.2.9 Chlorine dioxide Stock Solution preparation (1000 ppm as free chlorine)

Chlorine dioxide solution was prepared in the lab as per Standard Methods for the Examination of water and waste water, Method 4500-ClO_2 20^{th} Ed., APHA, 1998.

1. 63 ml of 5.25% sodium hypochlorite solution to one liter with DI water.
2. Add 8 ml of concentrated (12N) hydrochloric acid to 500 ml of water in a one liter volumetric flask. Mix and make up to volume with DI water (store in amber bottle).
3. Dilute 26 ml of technical sodium Chlorite solution 31.25% to one liter with DI water (store in amber bottle).
4. Pour 250 ml of dilute sodium hypochlorite solution into a one liter amber reagent bottle, to this add 250 ml of dilute hydrochloric acid solution and add 250 ml of dilute Sodium Chlorite solution. Make the solution to one liter.
5. Store the chlorine dioxide solution in a closed amber bottle in a Refrigerator.
6. Solutions of lower concentrations were freshly prepared from this stock solution as required.

4.2.10 Ozone Stock Solution preparation

1. Clean all glassware very well.
2. Add about 1 L of distilled / ultra-pure water in the special flask
3. Place the flask in the freezer for about 1 hour until the temperature reads about $2^{o}C$
4. Measure the concentration of ozone in the stock solution by ozone measuring kit from Ozone Solutions Inc., USA:
   - Zero the reader by the given ampoule included in the kit
   - Add 5 drops of the activation solution in the 25ml container

- Transfer 2.5 ml from the ozone stock solution into the 25 ml container
- Complete to the 25ml mark by adding ultra pure water.
- Use one of the ampoules to measure the ozone level. Break it inside the 25 ml container and wait few seconds until the ampoule is filled with the solution. Take it out, wipe with clean tissue paper and make a reading by the reader.
- Use the formula to calculate the ozone concentration (2.37 x Abs + 0.01)
- Multiply by a factor of 10 to determine the concentration of ozone in the stock solution.
- This solution can be used within couple of hours only. Always keep the stock ozone in the freezer to reduce the loss of ozone.

4. 3 Experimental Procedures

4.3.1 Part 1: Chlorination Methodology

Disinfection by chlorination was done according to the following experimental layout.

1. Blended water samples were prepared.
2. TOC was measured for all blended water samples.
3. The disinfectant was added to the blended water as per Table 7.
4. 30-50 ml of the samples was collected after reaction time of 24 and 48 hours (few drops of sodium sulphite were added in the sampling vials to quench the chlorine reaction).
5. 50 ml from each sample was collected to check total coliform by EPA Method 1604: Total Coliforms in Water by Membrane Filtration Using a Simultaneous Detection Technique.

6. Chlorine residual was measured using the DPD method after 24 and 48 hours (this was done before adding the sodium sulphite).
7. The samples were analyzed for TTHMs levels by GC-MS

Table 7. Experimental layout of chlorination

Experiment No.	Blending Ratio	Disinfection dose (ppm)	Temperature ^{o}C
1	1:2	1	25
2	1:2	2	25
3	1:2	5	25
4	1:2	5	35
5	1:2	5	45
6	1:5	1	25
7	1:5	2	25
8	1:5	5	25
9	1:5	5	35
10	1:5	5	45
11	1:10	1	25
12	1:10	2	25
13	1:10	5	25
14	1:10	5	35
15	1:10	5	45

4.3.2 Part 2: Chlorine Dioxide Methodology

1. Blended water samples were prepared.
2. Chlorine dioxide (disinfectant) solution was added to the blended water to get the exact concentration of the chlorine dioxide as per Table 8.
3. Collect 20-50 mL samples after reaction time of 24 and 48 hours (few drops of sodium sulphite were added in the sampling vials to quench the chlorine reaction).
4. Measure the chlorine residual using the DPD after 24 and 48 hours (this is done before adding the sodium sulphite).
5. Analyze the samples for chlorite by Ion Chromatography from Dionex using new EPA method.
6. 50 ml from each sample was collected to check total coliform by EPA Method 1604: Total Coliforms and Escherichia coli in Water by Membrane Filtration Using a Simultaneous Detection Technique.

4.3.3 Part 3: Ozonation Methodology

1. Blended water samples were prepared.
2. Preparation Stock solution of Ozone in cold water around (20 ppm) which used for spilicing blended water
3. Collect 5-10 ml samples after contact time of 0, 5, 10 and 20 minutes (few drops of sodium sulfate were added in the sampling vials to quench the ozone).
4. Measure the ozone residual using the kit.
5. Analyze the samples for bromide and bromate levels by Ion Chromatography.

6. 50 ml from each sample was collected to check total coliform by EPA Method 1604: Total Coliforms and Escherichia coli in Water by Membrane Filtration Using a Simultaneous Detection Technique.

Table 8. Experimental layout of disinfection by ClO_2

Experiment No.	Blending Ratio	Disinfection dose (ppm)	Temperature ^oC
1	1:2	1	25
2	1:2	2	25
3	1:2	5	25
4	1:2	5	35
5	1:2	5	45
6	1:5	1	25
7	1:5	2	25
8	1:5	5	25
9	1:5	5	35
10	1:5	5	45
11	1:10	1	25
12	1:10	2	25
13	1:10	5	25
14	1:10	5	35
15	1:10	5	45

Table 9. Experimental layout of ozonation

Experiment No.	Blended ratio	Disinfection Dose (ppm)	Temperature ^{o}C
1	1:2	0.5	25
2	1:2	1.0	25
3	1:2	2.0	25
4	1:2	5.0	25
5	1:2	2.0	15
6	1:2	2.0	45
7	1:5	0.5	25
8	1:5	1.0	25
9	1:5	2.0	25
10	1:5	5.0	25
11	1:5	2.0	15
12	1:5	2.0	45
13	1:10	0.5	25
14	1:10	1.0	25
15	1:10	2.0	25
16	1:10	5.0	25
17	1:10	2.0	15
18	1:10	2.0	45

4.4 Analytical Techniques

4.4.1 Total Trihalomethanes (TTHMs) Analysis by GC/MS

According to the Standard Methods all samples were analyzed based on the described procedures in APHA Standard Methods (APHA, 2003). Based on the direct aqueous injection, an Agilent 5890 series, GC high performance quadruple mass spectrometer (GC-MS) using a Purge and Trap technique (Fig. 4.1) was used for the identification and quantification of THMs. The calibration curve for GC/MS is shown in appendix A1, A2, A3 & A4.

Analytical conditions and equipment

The GC oven temperature was programmed from 40^{o}C (4minutes) to 140^{o}C at 8^{o}C/minutes. Other GCMS parameters were as follows:

- Column: J and W-DB5, 60m * 0.25 mm * 0.25µm thickness; Carrier Gas: Helium at 1.2 Ml/min.
- Injector Temp: 300^{0}C;
- SIM mode (Ions selected: 83, 85, 127, 129,171 and 173); MS Quad.
- Temp: 150^{0}C; MS Source temp

Figure 2: GCMS, Model HP 6890 & for MS HP 5973

4.4.2 Bromate, Chlorite and Bromide Analysis by Ion Chromatography

Bromate and chlorite in water was measured by ion chromatography using suppress conductivity detection according to U.S. EPA Method 300.1 B. An integrated Dionex ICS-3000 RFIC system equipped with an electrolytic eluent generator, an EluGen® EGC II KOH cartridge, a continuously regenerated anion trap column (CR-ATC), a dual piston pump with vacuum degas, with a 250 µL loop, a heated conductivity cell, and a column heater were all used in this work (Figure 4.2). An IonPac® AS19 (4 x250 mm) with its respective guard column, AG19 (4x50 mm), was used for all separations. Analytes were detected by suppressed conductivity with an ASRS® ULTRA II (4 mm) operating at 130 mA in the recycle mode. Chromeleon® 6.6 chromatography management software was used for system control and data processing. The calibration curve for IC is shown in appendix B1, B2 and B3.

Figure 3. Dionex ICS-3000 Ion Chromatography (IC) systems

4.4.3 Measurement of Total Organic Carbon (TOC)

TOC was measured for blended water sample with TOC analyzer (TOC 5000 A Shimadzu, (Figure. 4.3). The samples were acidified with HCl (1:1) for removing inorganic carbon then flushed by nitrogen for 10 minutes to remove CO_2. The calibration curve for TOC is shown in appendix C1.

Figure 4. TOC 5000 A Shimadzu.

4.4.4 Measurement of Residual Chlorine Analysis

Chlorine dosages and chlorine residual levels were measured by the standard [*N*,*N*-diethyl-P-phenylenediamine (DPD) method [APHA A,WEF, Standard Methods, 1998], by using Hach spectrophotometer 46700-00.

4.4.5 Measurement of Dissolved Ozone in Water

1. Clean all glassware very well.
2. Add about 1 L of distilled / ultra-pure water in the special flask
3. Place the flask in the freezer for about 1 hour until the temperature reads about $2^{o}C$
4. Measure the concentration of ozone in the stock solution by ozone measuring kit from Ozone Solutions Inc., USA:

- Zero the reader by the given ampoule included in the kit
- Add 5 drops of the activation solution in the 25ml container
- Transfer 2.5 ml from the ozone stock solution into the 25 ml container
- Complete to the 25ml mark by adding ultra pure water.
- Use one of the ampoules to measure the ozone level. Break it inside the 25 ml container and wait few seconds until the ampoule is filled with the solution. Take it out, wipe with clean tissue paper and make a reading by the reader.
- Use the formula to calculate the ozone concentration (2.37 x Abs + 0.01)
- Multiply by a factor of 10 to determine the concentration of ozone in the stock solution.
- This solution can be used within couple of hours only. Always keep the stock ozone in the freezer to reduce the loss of ozone.

CHAPTER 5

RESULTS AND DISCUSSION

5.1 Disinfection of Blended Water Samples by Chlorination

5.1.1 Effect of blending ratio on the formation of THMs

The results showed that brominated THMs (i.e. bromoform ($CHBr_3$) and dibromochloromethane ($CHBr_2Cl$) are the dominant components of the THMs formed in all water formulations disinfected by chlorination (Fig. 5.1). In fact, results showed that bromoform represents more than 80% of the total THMs formed in the blended water samples regardless of the different mixing ratios or levels of chlorine dosage. On the other hand, chlorinated THMs (i.e. chloroform) was not detected in most of the samples. This is mainly due to the original high levels of bromide ion (Br^-) in brackish which were also detected in the blended water samples in the range of 0.25 to 0.98 ppm as shown in Table 6. The absence of chlorinated THMs can be attributed to the low levels of TOC levels which range from 0.056 to 0.098 ppm only.). Brominated and iodinated DBPs are particularly problematic because they often are more carcinogenic or mutagenic than their chlorinated analogs [S.D. Richardson, et al. 2003 and M.J. Plewa and E.D. Wagner, 2004). The formation of brominated disinfection by-products was attributed to the conversion of hypochlorous acid to hypobromous acid, which occurs through an acid-catalyzed reaction (K. Kumar and D.W. Margerum, 1987).

It was also observed that as the proportions of product water in the blended water samples increased compared to groundwater, less brominated and more chlorinated THMs were detected. Bromoform levels were found to decrease and chloroform levels increase as the product proportion in the blended water increased from 2 to 10 as shown in Figure 5.2. This is attributed to the fact that the source of bromide ion which is responsible in forming brominated THMs is the brackish groundwater.

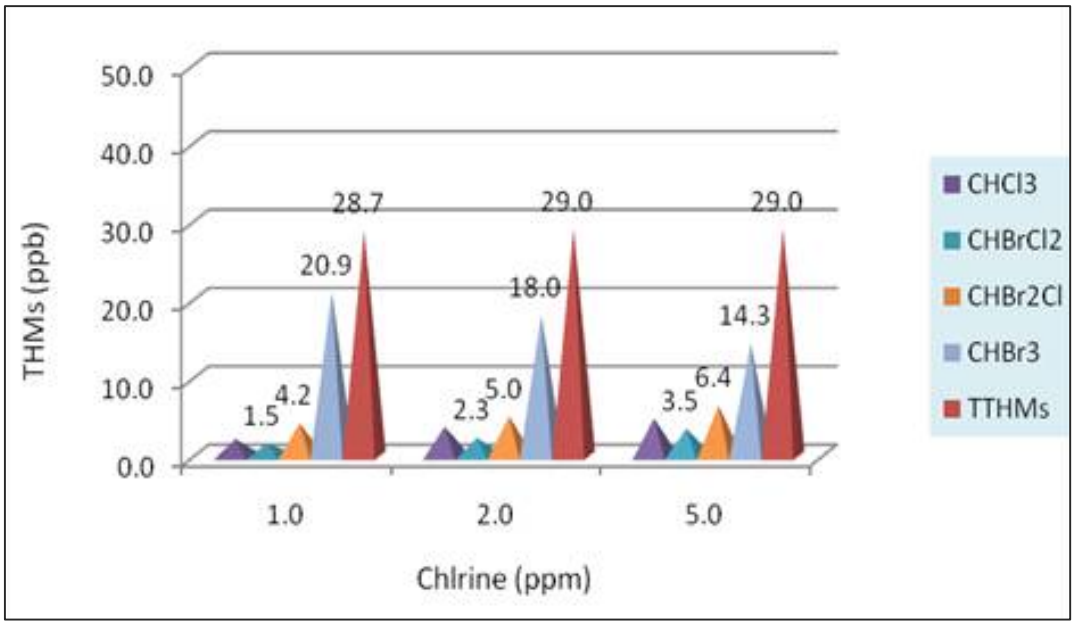

Figure 5. THMs Levels (ppb) in blended water of 1:10 Ratio, pH =7, and Temp. =25°C after dosing with Cl_2 of 1, 2, and 5 ppm and reaction time = 24 hrs

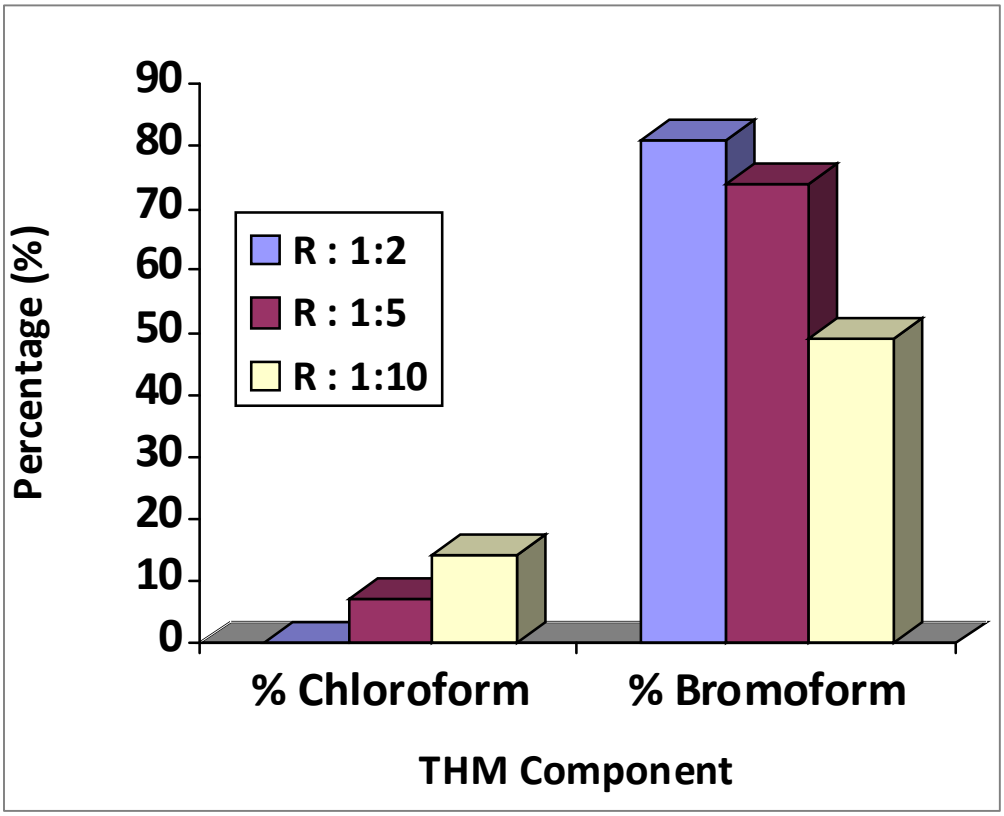

Figure 6. Percentages of Chloroform and Bromoform in Blended Water Samples at Cl_2 = 5 ppm

5.1.2 Effect of chlorine dosage on the formation of THMs

Results of analysis of THMs measured at 25^{o}C after 24 Hrs of dosing at different blending ratios are shown in Figure 5.3. From figure, it was observed that with dose rate the formation of THMs increases at the ratio 1:2 and 1:5 whereas at ratio 1:10 no change in the formation of THMs noticed. However, it is noticed that even at much high levels of chlorine dosage of 5 ppm which is much higher than the usual dosage, levels of THMs formed are much lower than the maximum allowable limit of THMs of 80 ppb. This clearly showed that the current practice of disinfecting blended water samples by chlorine is not expected to lead to the formation of harmful THMs if consumed within 24 hours and water temperature do not exceed 25^{o}C. This result also showed that if we increase the blending ratio 1:10 and above there is no further increase in THMs formation. From the present study ratio 1:10 was found to be ideal for control of THMs formation at chlorine dosage rate of 1, 2 and 5 ppm.

5.1.3 Effect of temperature on the formation THMs

Different batches of blended water samples were treated with three levels of chlorine of 1, 2 and 5 ppm. Temperatures of blended water samples were set at three levels of 25, 35 and 45^{o}C using water circulation bath. Samples were then collected after 24 hours and analyzed for THMs in blended water samples. Effect of temperature for the highest dosage rate of chlorine (5 ppm) was studied (Figure 5.4). This dosage rate of chlorine was selected in this study because at 25^{o}C for 1:10 ratio no effect of dosage was observed.

Results clearly indicated that temperature has a significant effect on the formation of THMs in blended water samples. For example, TTHMs levels increased from around 29

to 138.5 ppb when the temperature increased from 25 to 45^{o}C in water samples blended with 1:10 brackish to product water. Similarly, TTHMs increased from 40.5 to 171.8 ppb and from 42.6 to 175.5 ppb when the temperature increased from 25 to 35^{o}C for a blending ratio of 1:5 and 1: 2 respectively. The TTHMs levels formed at 45^{o}C in the three blending ratios dosed with 5 ppm chlorine is much higher than the USEPA MCL levels of TTHMs of 80 ppb.

5.1.4 Effect of time on the formation of THMs

Different batches of blended water samples were treated with 2 ppm of chlorine and were analyzed after 24 and 48 hours to study the effect of contact time on the formation of THMs in blended water samples. Figure 5.5 shows the effect of time on the formation of THMs at different blending ratio at 25^{o}C. All the blending ratios showed an increase in the THMs formation with time. Further at higher temperature all the blending ratio at 5 ppm dosing showed high levels of THMs formation (Figure 5.6). Also, comparing with the values at 25^{o}C and 2 ppm dosage the values of THMs are found to be above the maximum regulated values. This showed that at higher dosage rate of chlorine and at higher temperature there is an increase in THMs formation. From the Figure 5.6 it is also observed that THMs formation is very high at ratio 1:2 and 1:5 after 24 and 48 hours whereas at 1:10 ratio lower values were observed. These results also confirm previous results by other researchers which show that formation of DBPs is time dependent. But longer contact time than 48 hours may lead to the decrease of THMs levels due to the fact that THMs are semi-volatile compounds and may evaporate during the transport and storage in the main distribution systems.

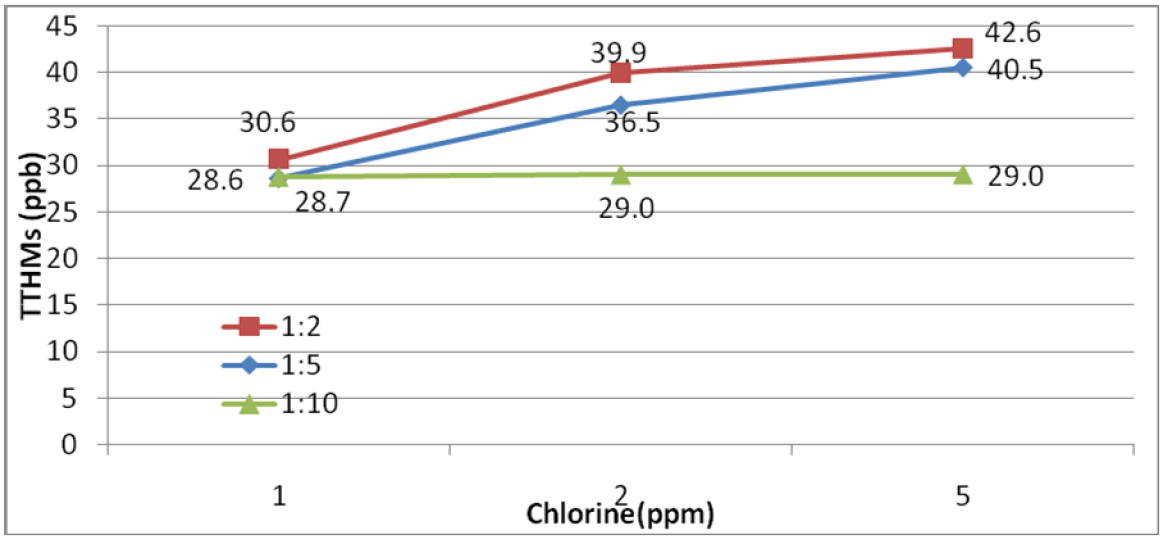

Figure 7. Effect of chlorine dosage on the formation of THMs at 25°C after 24 hours

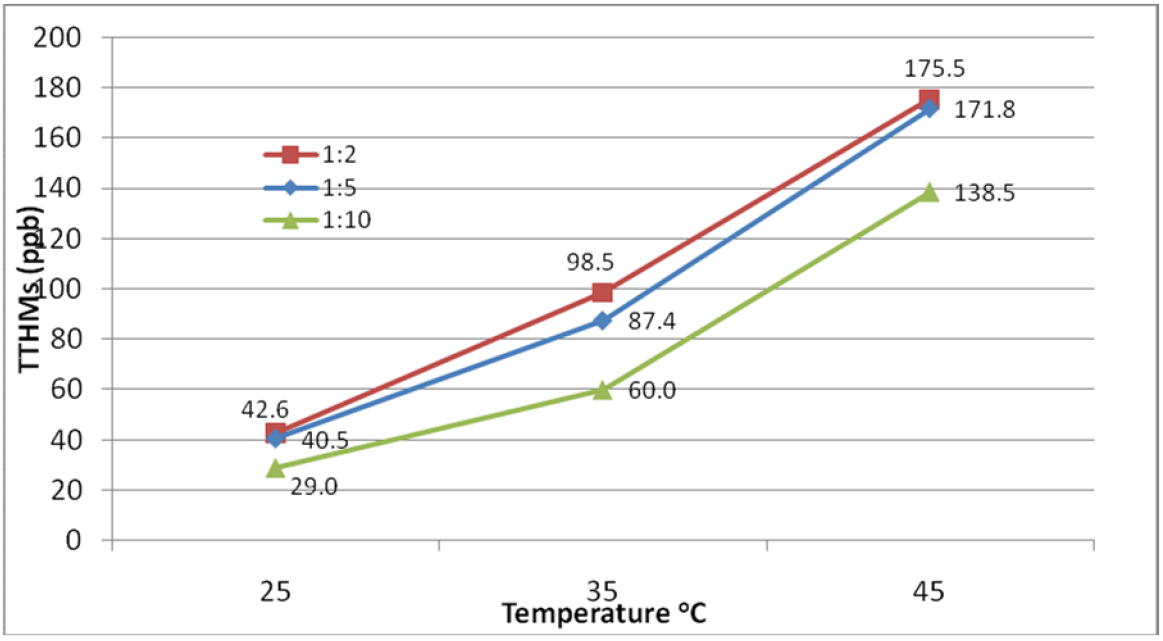

Figure 8. Temperature Effect on the formation of TTHMs at different blending ratio at 5 ppm and after 24 hours

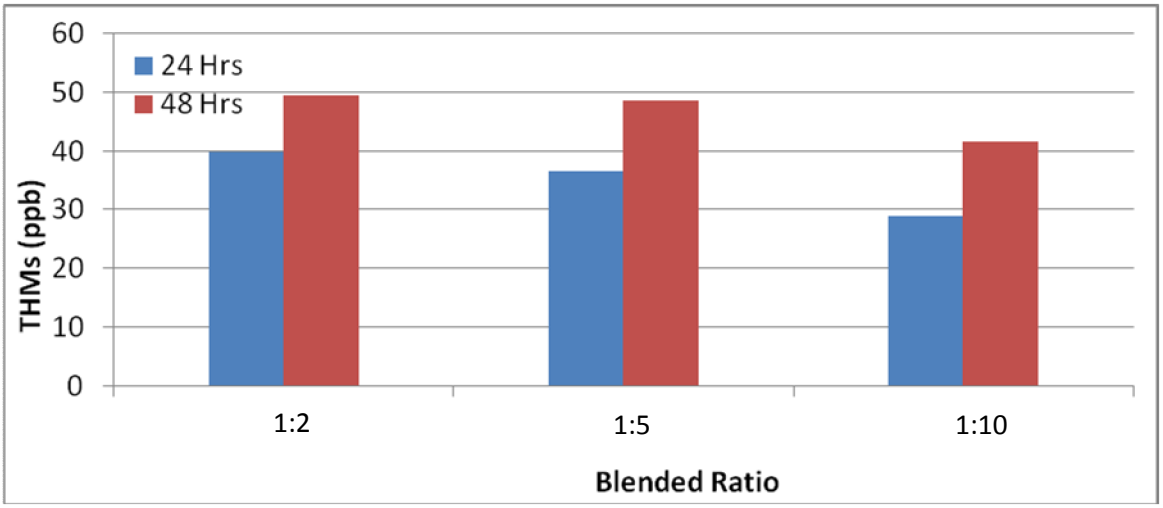

Figure 9. Effect of Time on the formation of TTHMs at different blending ratio at 25°C and 2 ppm chlorine

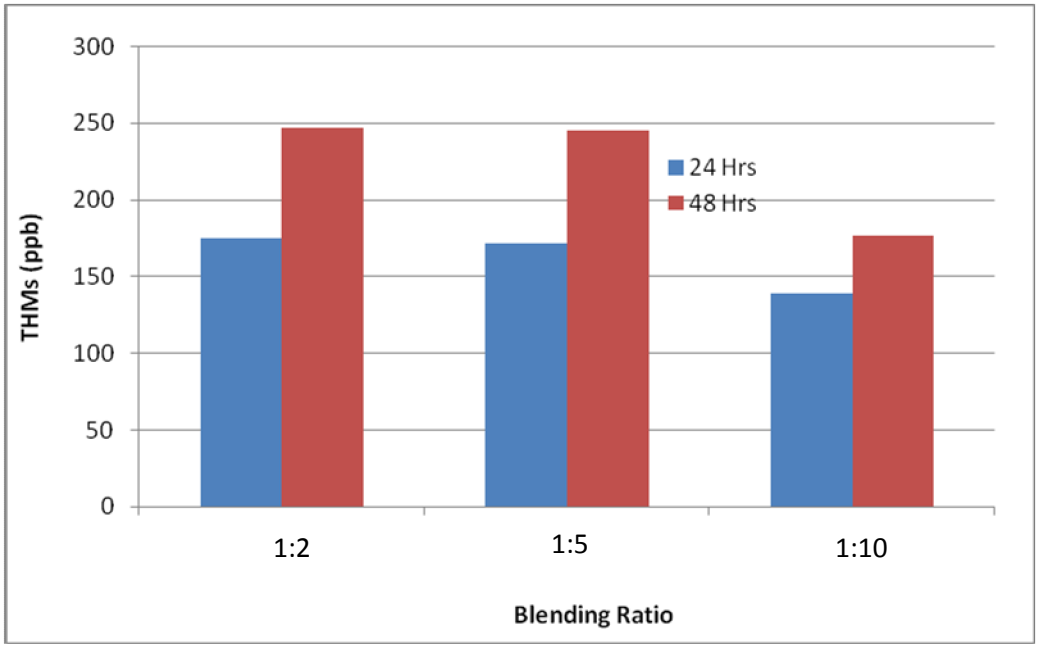

Figure 10. Effect of Time on the formation of TTHMs at 45^{o}C and 5 ppm Chlorine

5.2 Disinfection of Blended Water Samples by Chlorine Dioxide

5.2.1 Effect of blending ratio and chlorine dioxide dosage on the formation of Chlorite at 25°C

The effect of blending ratios on chlorite formation in blended water samples investigated showed low chlorite levels with blended ratios of 1:2 and 1:5 and was found to increase with chlorine dioxide dosage of 1 to 5 ppm (Figure. 5.7). But very low levels of chlorite were formed in water samples blended with a ratio of 1:10, while as high as 0.25 ppm of chlorite was formed with higher brackish (groundwater) portions (i.e. for ratios 1:2 and 1:5).

5.2.2 Effect of Temperature on the Formation of Chlorite at 5 ppm ClO_2

The effect of temperature of blended water samples on chlorite formation in blended water samples was also investigated in this study. Results shown in (Figure 5.8) depict no effect of temperature on the formation of chlorite in blended water samples. This was even true irrespective of the blending ratio used for preparing the blended water samples. For example, for a blending ratio of 1:5, the chlorite concentration levels detected were constant at 0.26 ppm.

5.2.3 Effect of Reaction Time on the Formation of Chlorite at 5 ppm ClO_2

In this study, the effect of reaction time on the formation of chlorite in blended water samples was investigated. Results shown in (Figure 5.9) indicate a noticeable effect of reaction time on the chlorite levels in blended water samples. In fact comparing (Figure 5.8 and 5.9) indicate a marginal decrease of chlorite after a reaction time of 48 hours.

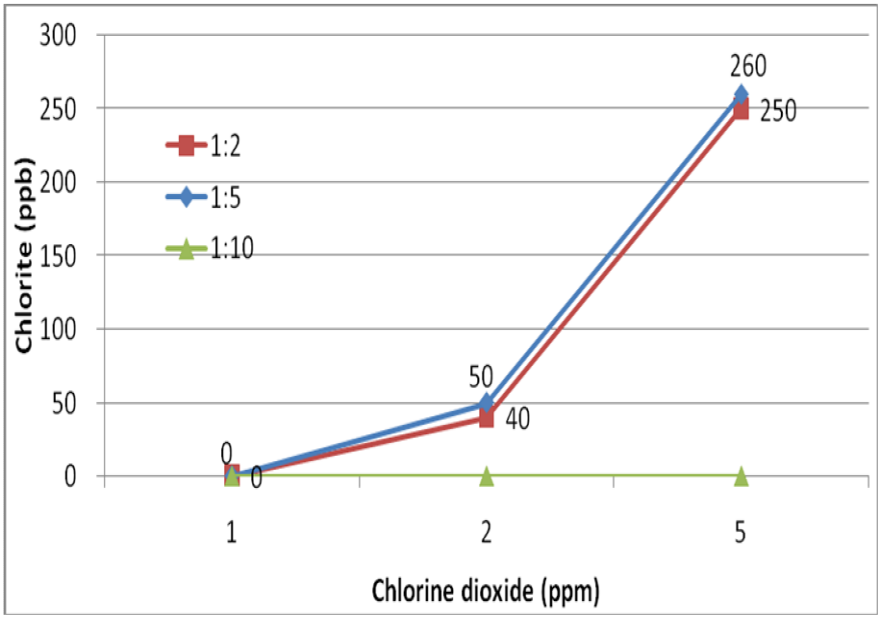

Figure 11 : Chlorite Levels (ppm) in water blended at different ratios ,pH =7, and Temp. =25^{o}C after dosing with ClO_2 of 1,2, and 5 ppm and Reaction Time = 24 hrs

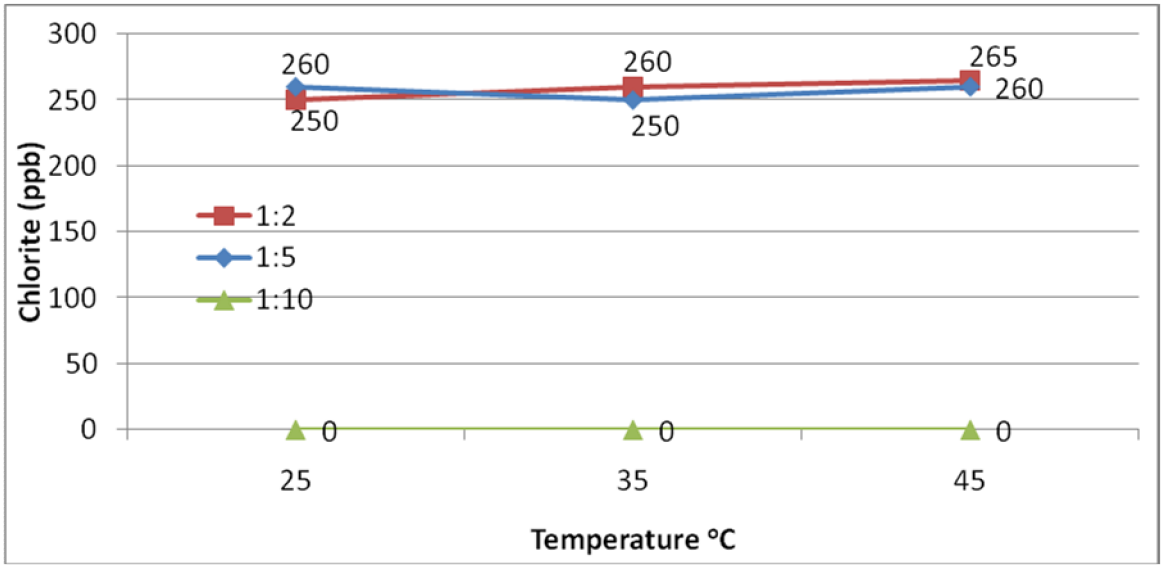

Figure 12: Chlorite Levels (ppm) in waters blended at different ratios with pH =7, and ClO_2 Dose = 5 ppm at Different Temperatures and Reaction Time = 24 hrs

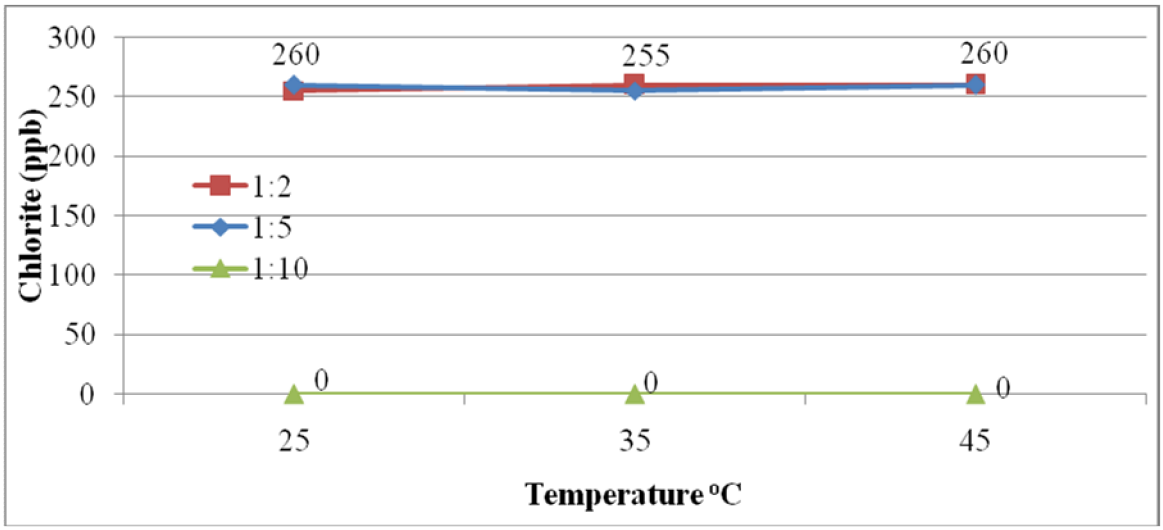

Figure 13: Chlorite Levels (ppm) in blended water, pH =7, and Temp. =25 C after dosing with ClO_2 of 1, 2, and 5 ppm and Reaction Time = 48 hrs

5.3 Disinfection of Blended Water Sample by Ozonation

5.3.1 Effect of Blended Water Sample and Ozone dosage on the formation of Bromate

In (Figure 5.10, 5.11 and 5.12) bromate formations at pH 7 are shown as a function of the ozone dosage at 5, 10 and 20 minutes contact time at 25^{o}C and different blending ratios. In sample collected after 5 minutes, there is a very similar and linear increase in bromate concentration with increasing ozone contact time. With an ozone dose of 1ppm, bromate concentrations are not detected , at 2 ppm dosage the bromate concentrations were around 10 ppb (which is close to the drinking water standard). At 5 ppm ozone dosage the bromate concentrations were very high (260 ppb). The results show that lower ozone dosage is best suited for keeping the bromate concentrations in the drinking water standard levels.

In samples collected after 10 and 20 minutes contact time, there is a very similar and linear increase in bromate concentration with increasing ozone contact time as seen with 5 minutes contact time except that the values of bromate concentrations are a little more but still in the drinking water limits. At 5 ppm of ozone dosage for all blending ratios and at 5, 10 an 20 minutes contact time the bromate concentration were very high (185, 220 and 260 ppb) indicating that the higher ozone dosages were not suitable for disinfection. Using the lower ozone dose is thus advantageous to almost completely suppress bromate formation. (Laurence Meunier, et.al, 2006).

5.3.2 Effect of Temperature on the formation of Bromate

In waters with bromide levels above 50 µg/l bromate formation may exceed the drinking water standard of 10 µg/l under certain treatment conditions [von Gunten, et.al, 2000]. One of the decisive factors is the temperature of the treated water. By increasing temperature, both the efficiency of inactivation of microorganisms and bromate formation increase. Therefore, it has to be tested whether lower or higher temperatures lead to a better performance with regard to the overall process (sufficient disinfection with low bromate). In (Figure 5.13, 5.14 and 5.15) bromate formations at pH 7 are shown as a function of temperature at 5, 10 and 20 minutes contact time at 2 ppm ozone dosage and different blending ratios. The BrO_3^- concentrations are lower than 10µg/l at the lower temperature. At 1:10 blending ratio the bromate concentrations are found to be lower than ratios 1:2 and 1:5 due to the lower bromide concentrations (Table 6).

At 15^oC bromated concentrations are not detected (except for the blending ratio 1:2), at 2 ppm dosage the bromate concentrations were around 10 ppb (which is close to the

drinking water standard), and the bromate concentrations at 45^{o}C were very high. Increased temperature has shown to increase the rate of bromate formation as a result of increased reaction kinetics and because the equilibrium between $HBrO_3 \rightarrow BrO^- + H^+$ shifts to the right as the temperature increases due to a commensurate increase in the acidity constant (Legube et., al 2004).

5.3.3 Effect of Contact Time on the formation of Bromate

In (Figure 5.16 and 5.17) bromate formations at pH 7 is shown as a function of contact time at 25 and 45^{o}C at 2 ppm ozone dosage and different blending ratios.

In samples collected at 25^{o}C and 45^{o}C there is a similar and linear increase in bromate concentration with increasing contact time. The bromate concentrations vary with blending ratios and show a decreasing trend from 1:2 to 1:10. Further it is noticed that at 25^{o}C the bromate concentrations at all the blending ratios were around 10 ppb which is close to the drinking water standard.

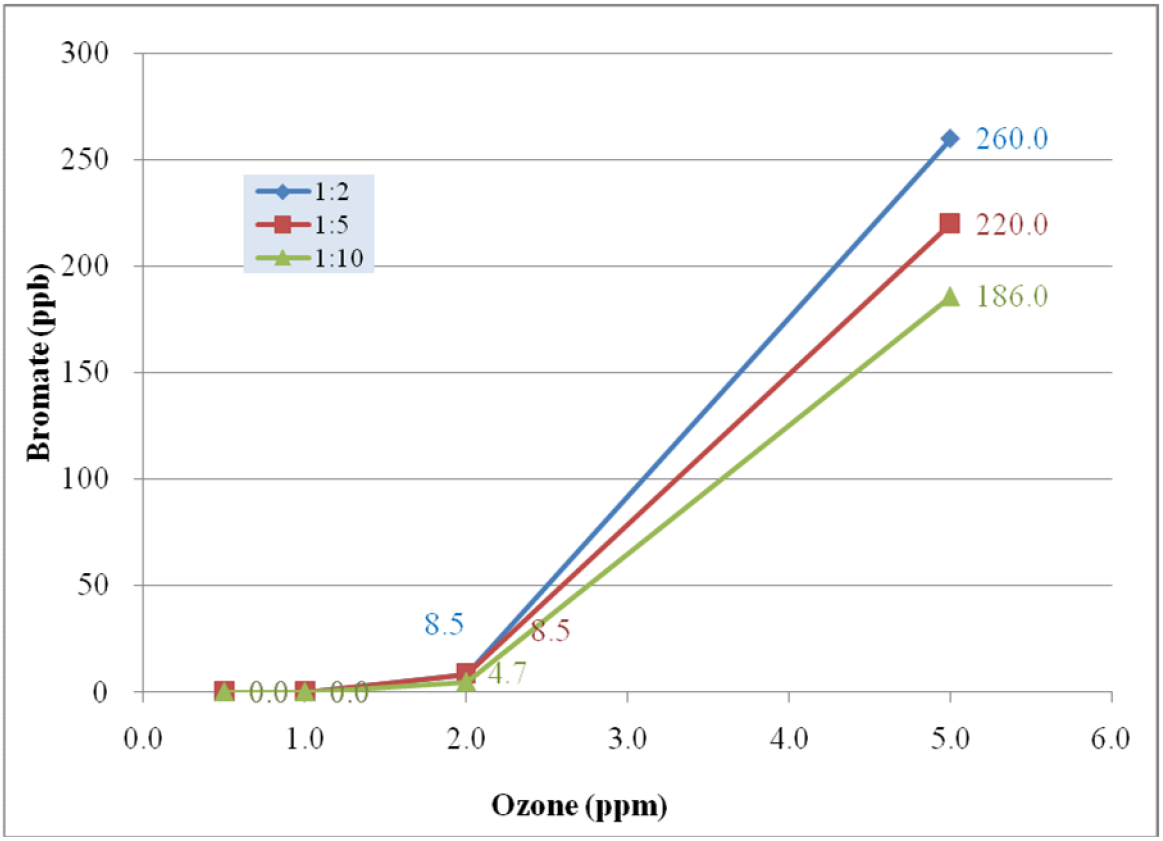

Figure 14. Effect of Ozone dosage on the formation of Bromate at 25°C after 5 minutes contact time.

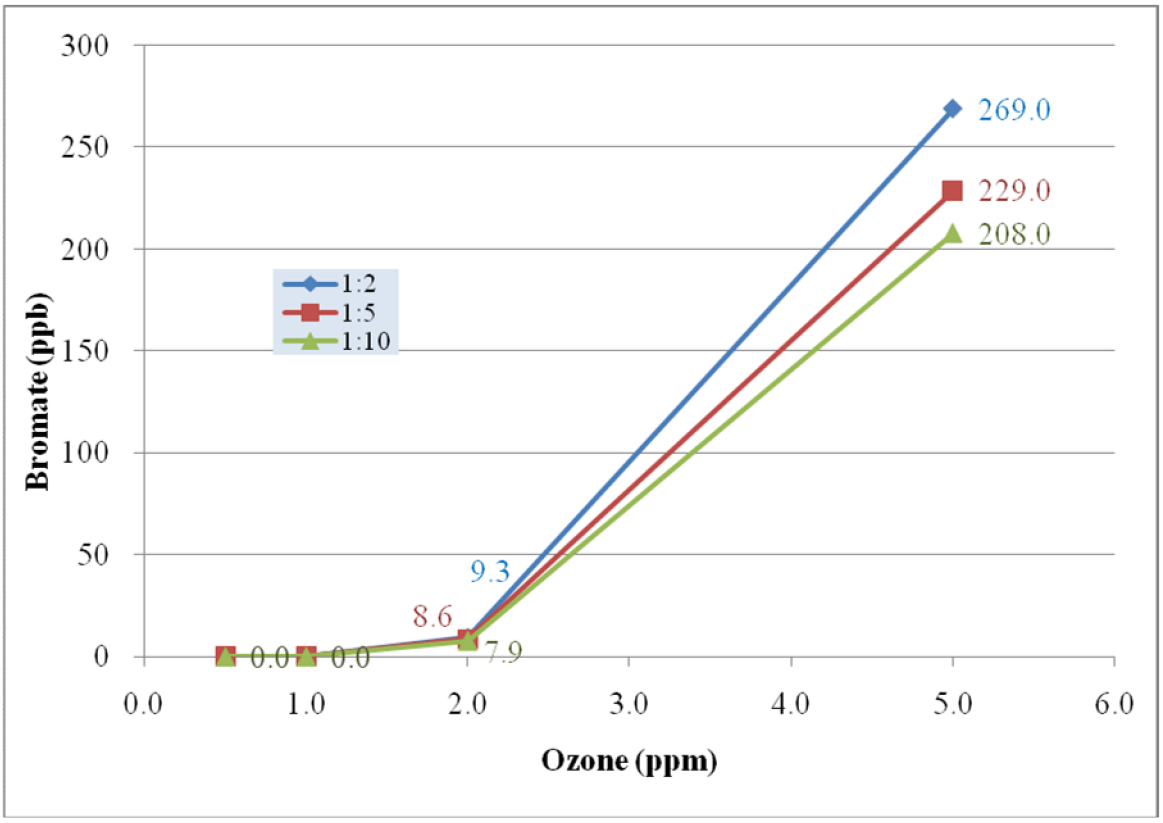

Figure 15. Effect of Ozone dosage on the formation of Bromate at 25^{o}C after 10 minutes contact time.

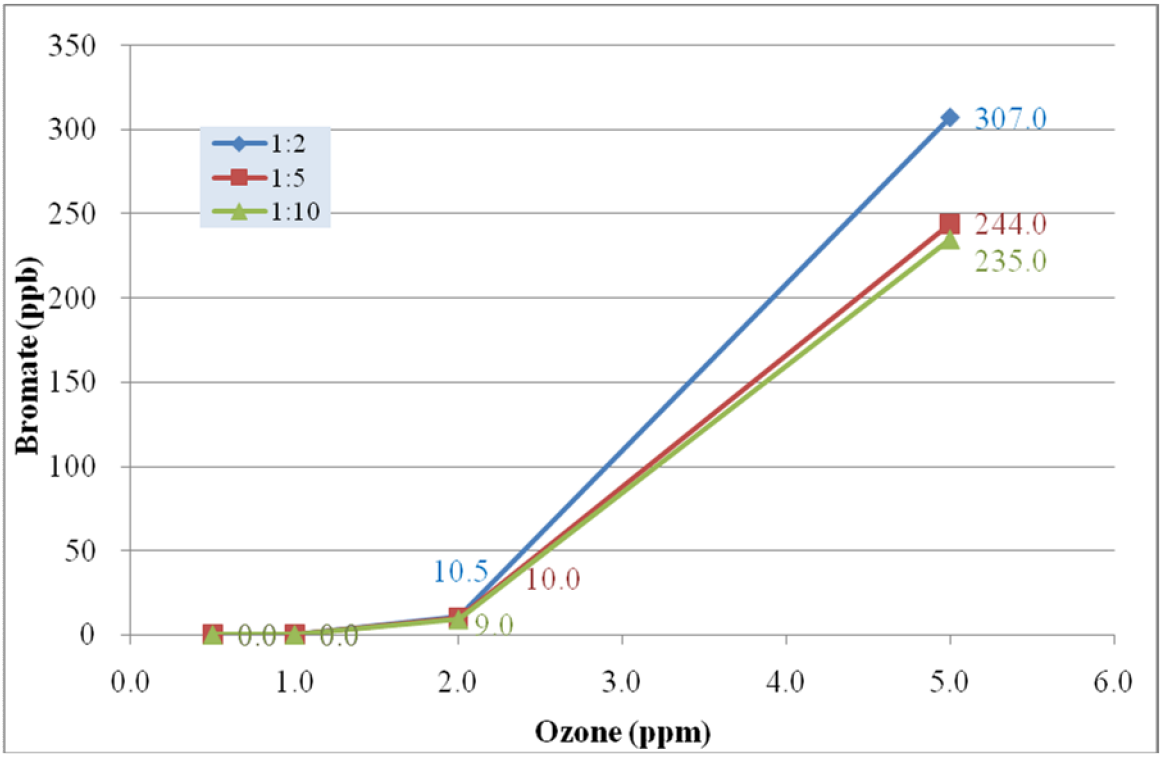

Figure 16: Effect of Ozone dosage on the formation of Bromate at 25°C after 20 minutes contact time.

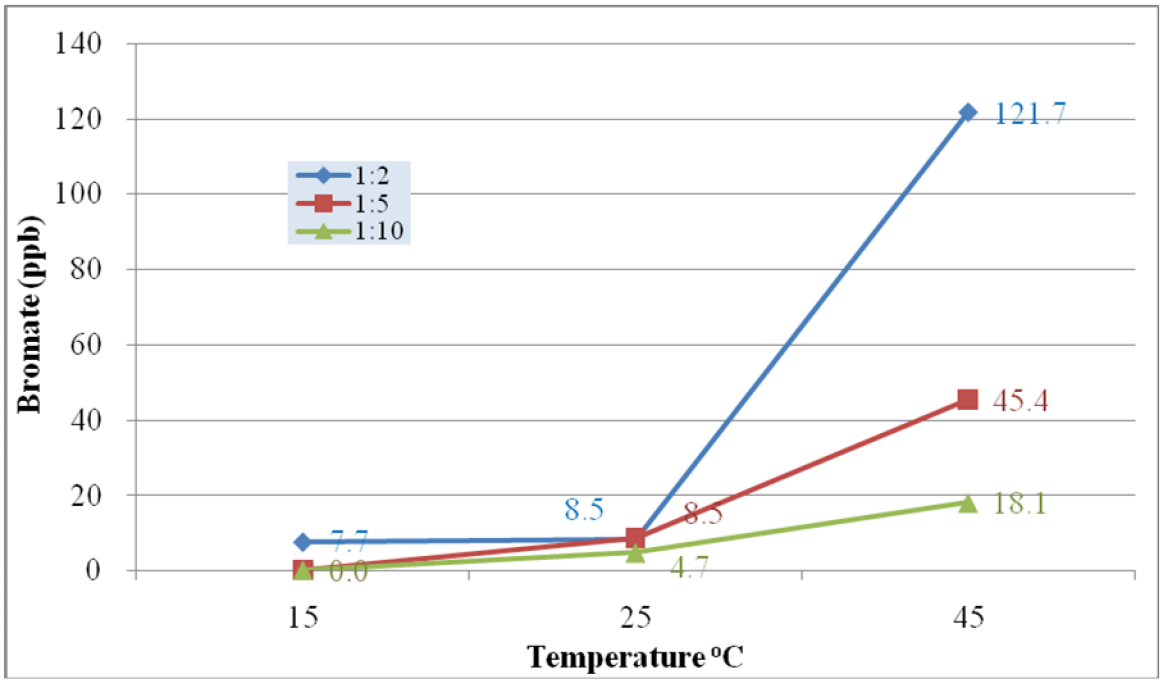

Figure 17. Effect of Temperature on the formation of Bromate at 2ppm after 5 minutes contact time.

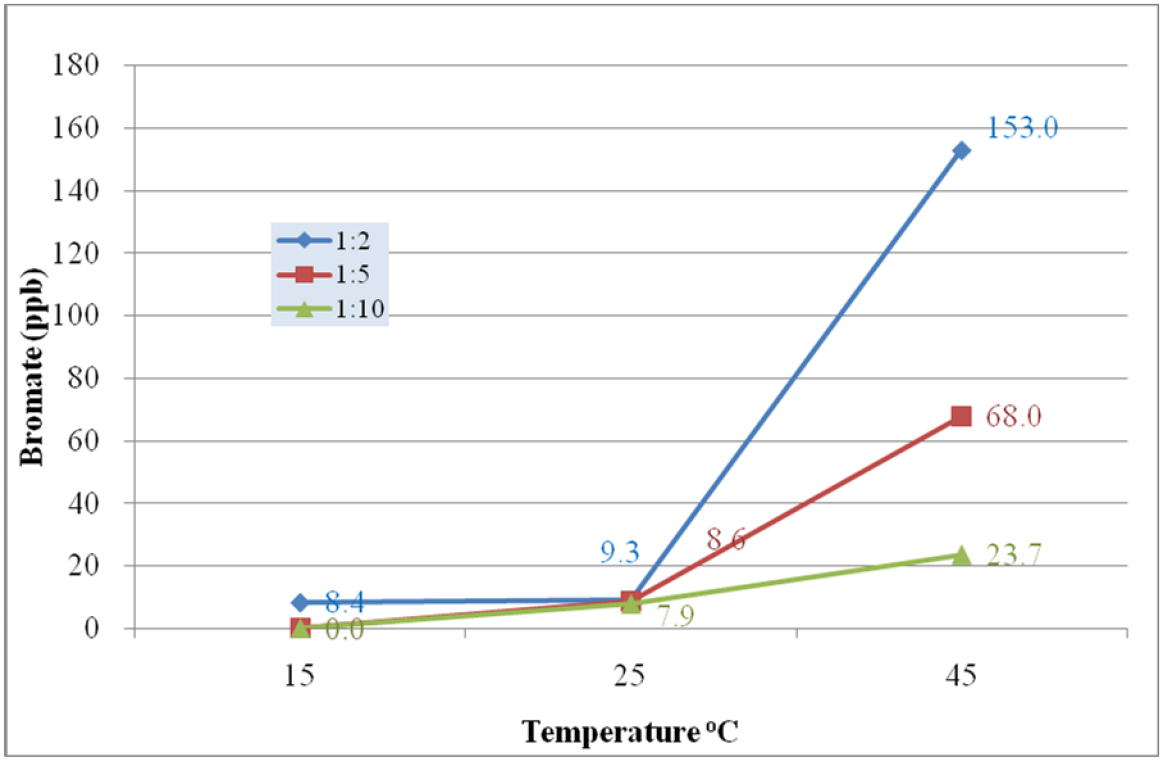

Figure 18. Effect of temperature on the formation of bromate at 2ppm after 10 minutes contact time.

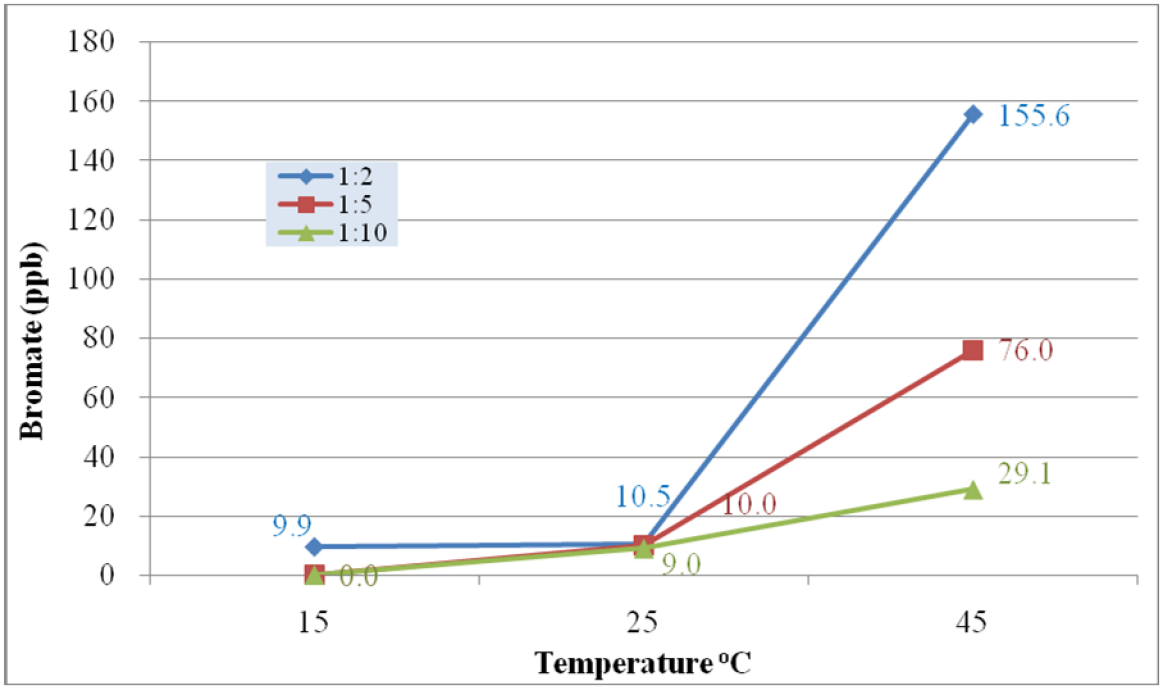

Figure 19. Effect of temperature on the formation of Bromate at 2ppm after 20 minutes contact time.

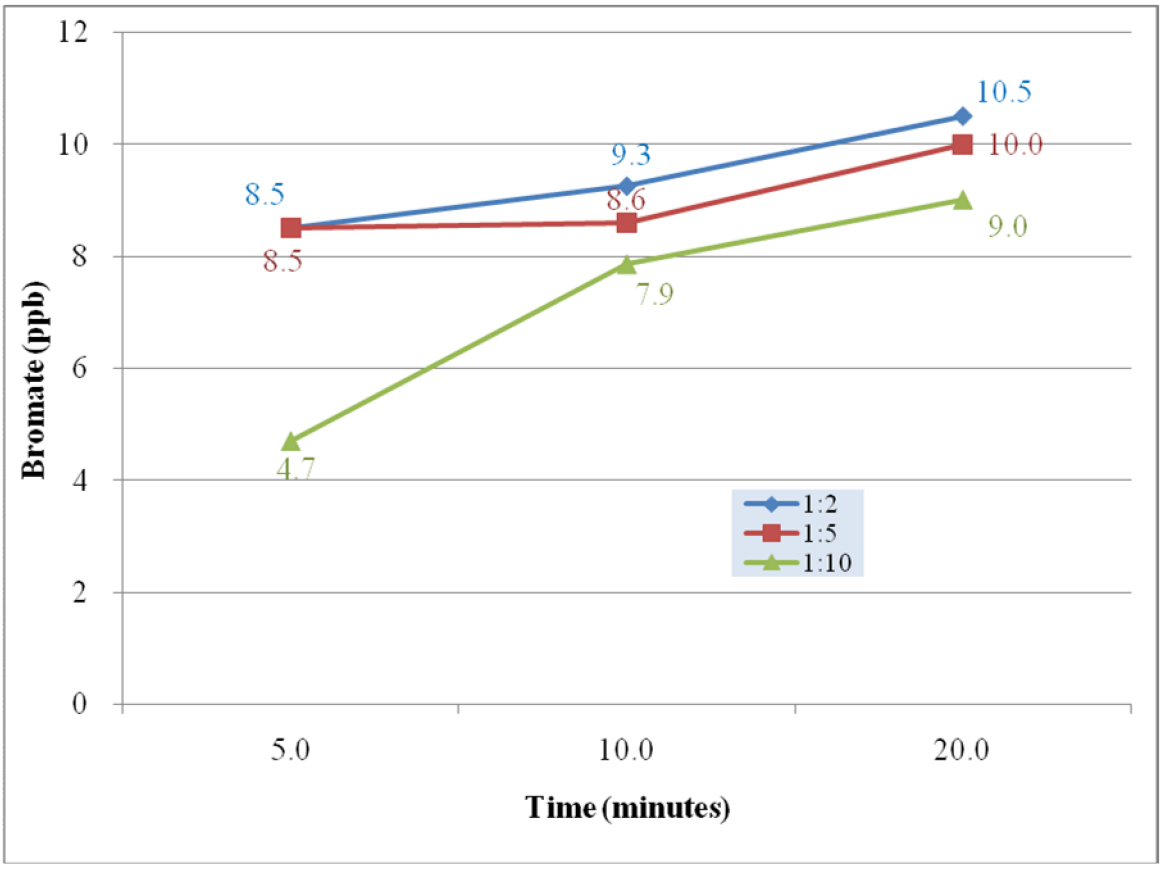

Figure 20. Effect of contact time on the formation of Bromate at 2ppm at 25°C

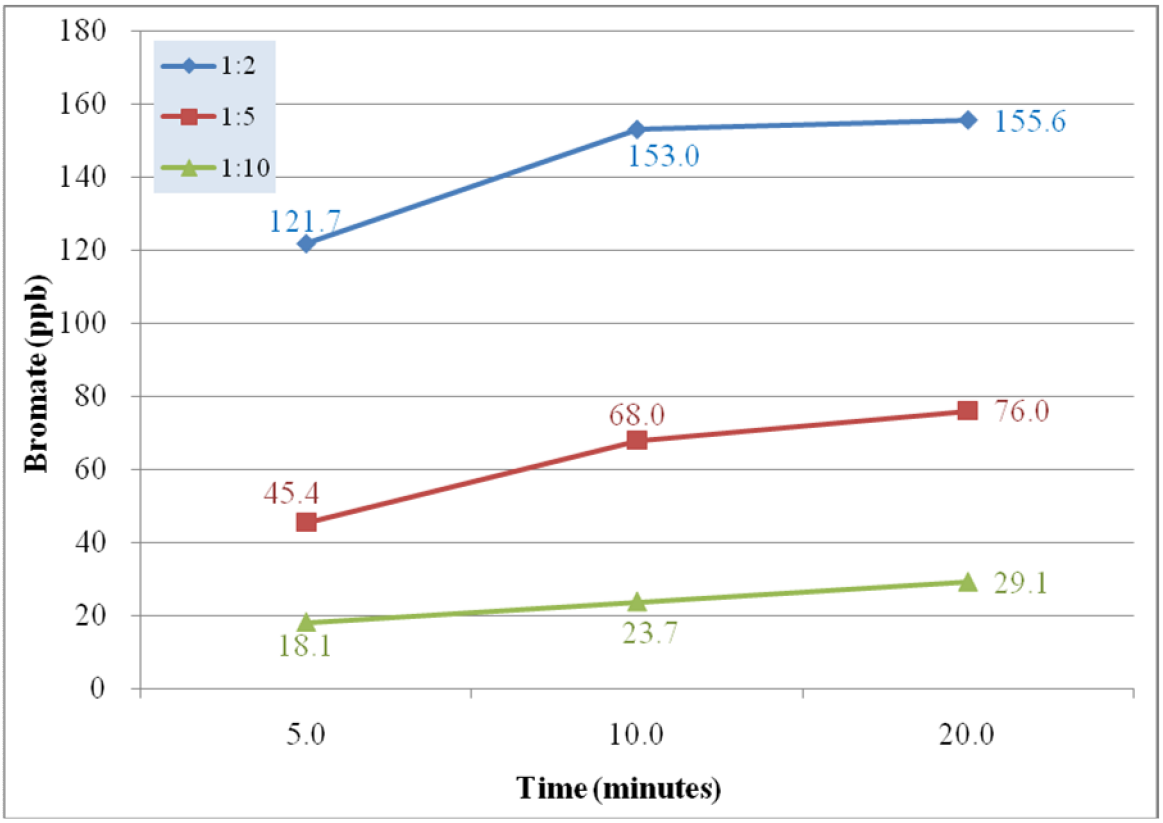

Figure 21. Effect of contact time on the formation of Bromate at 2ppm at 45°C

CHAPTER 6

SUMMARY & CONCLUSIONS

The main objective of this study was to investigate the fate of DBPs formed when using three disinfectanat (i.e Cl_2, ClO_2 and O_3) in blended water. The by-products resulted from these disinfection processes were quantified under different treatment conditions of disinfectant dosage, temperature and reaction time. The correlation between the type of by-products formed and the quality of the source water (desalinated seawater and groundwater) were also investigated in this study.

In the first part, the study with chlorine revealed that total Trihalomethanes (TTHMs) formation increases 0 to 247 ppb as chlorine dosages increases from 1 to 5 ppm at 25^{o}C. The blending ratio of 1:10 (v/v, raw: desalinated) showed the lowest THMs formation at chlorine dosage of 1, 2 and 5 ppm. Bromoform ($CHBr_3$) and dibromochloromethane ($CHBr_2Cl$) were the dominant components of the THMs formed in all water formulations disinfected by chlorination. In fact, results show that bromoform represents more than 80% of the total THMs formed in the blended water samples regardless of the different mixing ratios or levels of chlorine dosage. On the other hand, chloroform was not detected in most of the samples. This is mainly due to the original high levels of bromide ion (Br^-) in brackish which were also detected in the blended water samples in the range of 0.25 to 0.98 ppm. It was observed that with dose rate the formation of TTHMs increases at the ratio 1:2 and 1:5 whereas at ratio 1:10 no change in the formation of

TTHMs was noticed. However, even at much high levels of chlorine dosage of 5 ppm, levels of THMs formed were much lower than the maximum allowable limit of TTHMs of 80 ppb. In the present study blending ratio 1:10 was found to be ideal for control of TTHMs formation at chlorine dosage rate of 1, 2 and 5 ppm. Results also showed an increase of TTHMs formation with increasing temperature at 5 ppm. TTHMs levels were found to increase from around 29 to 138.5 ppb when the temperature increased from 25 to 45^{o}C in water samples blended with 1:10 brackish to product water. Similarly, TTHMs increased from 40.5 to 171.8 ppb and from 42.6 to 175.5 ppb when the temperature increased from 25 to 35^{o}C for a blending ratio of 1:5 and 1: 2 respectively.

In the second part, low chlorite levels resulted from chlorine dioxide disinfection of blended water with blending ratios of 1:2 and 1:5 at 25^{o}C was found to increase with dosage of 1 to 5 ppm. But, chlorite species were not detected at blending ratio of 1:10. Results also showed no effect of temperature and time at 5 ppm on the formation of chlorite in blended water samples irrespective of the blending ratio used.

Third part of the study, results with disinfection by ozone showed that bromate formation increased with increase in ozone dosages from 1 to 5 ppm at 25^{o}C and reaction time from 5 to 20 min. At 5 ppm of ozone dosage for all blending ratios and at 5, 10 an 20 minutes contact time the bromated concentration were very high indicating that the higher ozone dosages were not suitable for disinfection. Using the lower ozone dose is thus advantageous to almost completely suppress bromate formation.

At 15^{o}C bromated concentrations are zero (except for the blending ratio 1:2), at 2 ppm dosage the bromated concentrations were around 10 ppb (which is close to the drinking water standard), and the bromate concentrations at 45^{o}C were very high.

A linear increase in bromate concentrations was observed with increasing contact time at 25 and 45^{o}C at 2 ppm dosage. The bromate concentrations were found to vary with blending ratios and showed a decreasing trend from 1:2 to 1:10. Further it was noticed that at 25^{o}C the bromate concentrations at all the blending ratios were around 10 ppb which is close to the drinking water standard.

In summary, the following conclusions were reached at the end of this research:

1. The blending ratio of 1:10 (v/v, raw: desalinated) showed the lowest THMs formation at chlorine dosage of 1, 2 and 5 ppm.

2. Temperature has a significant effect on the formation of THMs and Bromate in blended water samples but no effect on the formation of Chlorite.

3. THMs formation is very high at ratio 1:2 and 1:5 after 24 and 48 hours whereas at 1:10 ratio lower values were observed.

4. All the blending ratios showed an increase in the THMs formation with time.

5. At higher temperature all blending ratio at 5 ppm dosing show high levels of TTHMs formation.

6. In the present study blending ratio 1:10 was found to be ideal for control of THMs formation at chlorine dosage rate of 1, 2 and 5 ppm.

7. Blending ratios 1:2 and 1:5 with high dosage of chlorine dioxide is affected on the formation of chlorite.

8. There is a very similar and linear increase in bromate concentration with increasing ozone contact time.

9. With an ozone dose of 1ppm, bromated concentrations are zero and at 2 ppm dosage the bromated concentrations were around 10 ppb (which is close to the drinking water standard) but, at 5 ppm ozone dosage the bromated concentrations were very high.

10. Lower ozone dosage is best suited for keeping the bromate concentrations in the drinking water standard levels.

11. At 5 ppm of ozone dosage for all blending ratios and at 5, 10 an 20 minutes contact time the bromated concentration were very high indicating that the higher ozone dosages were not suitable for disinfection.

12. At 1:10 blending ratio the bromate concentrations are found to be lower than ratios 1:2 and 1:5 due to the lower bromide concentrations.

CHAPTER 7

RECOMMENDATIONS

The main outcome of this study revealed that disinfection process is an essential water treatment process that has to be fully investigated. Adopting certain disinfectant largely depends on many factors including: water quality (i.e. blending ratio), chemical and physical characteristics of the treated water, type, dosage and efficiency of the disinfectant, the treatment conditions (i.e. temperature and contact time) as well as the fate of the disinfection by-products (DBPs) formed. Careful design of the disinfection process is necessary to balance between the benefit from removing pathogenic germs from water sources and at the same time do not cause the formation of hazardous disinfection by-products (DBPs).

There are still a number of issues related to disinfection of blended water that need to be studied, therefore it is highly recommended that additional studies to be conducted in this regard that can address issues like:

- Comparing the killing efficiency of different types of pathogenic germs using different disinfectants used for blended waters.
- Assessing the fate of chlorite and chlorate formation in blended waters when chlorine dioxide is generated on site by different techniques.
- Conduct similar studies for bottled drinking water samples as well.

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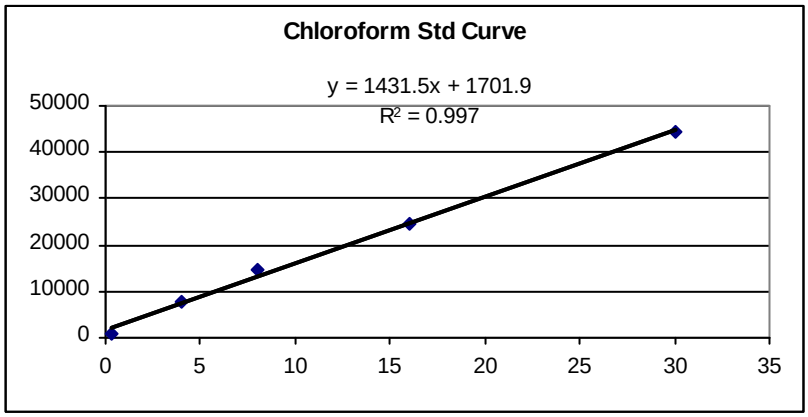
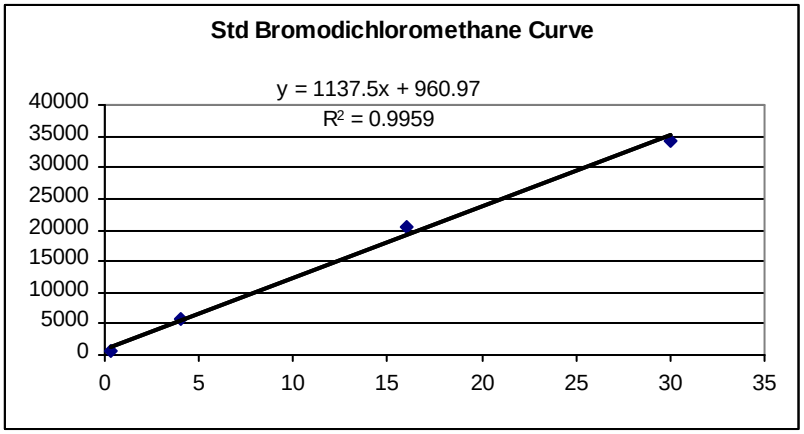
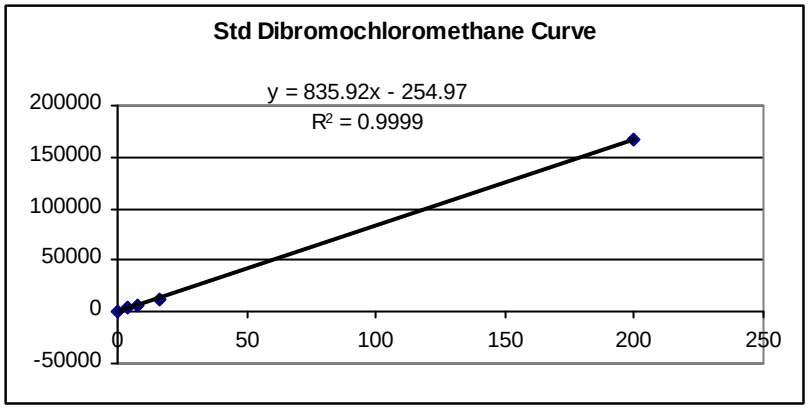
APPENDICES

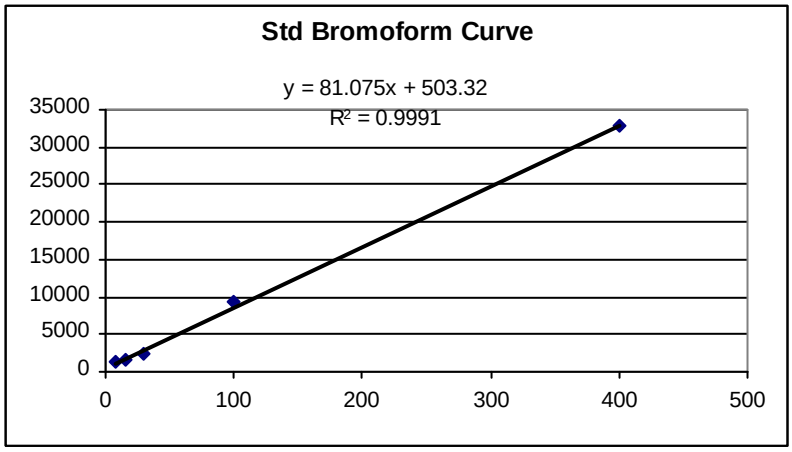
APPENDIX A

CALIBRATION CURVE OF THMs


Chloroform Std Curve
y = 1431.5x + 1701.9
R² = 0.997
50000
40000
30000
20000
10000
0
0
5
10
15
20
25
30
35

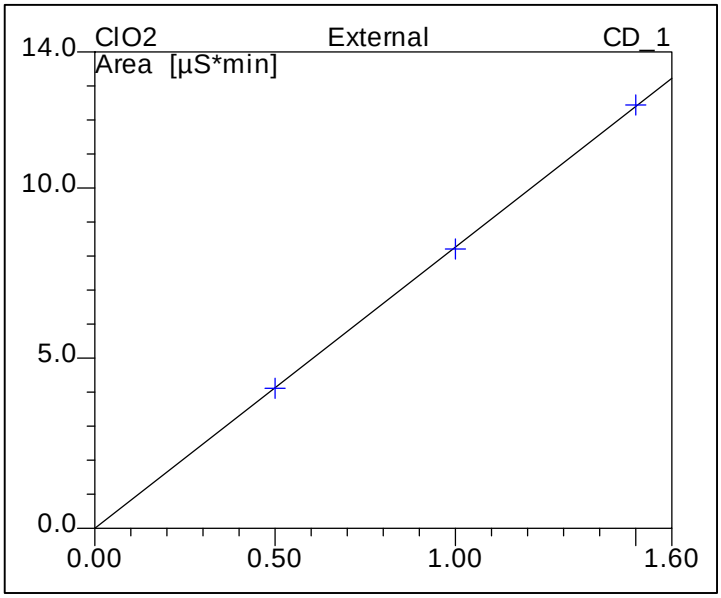

Std Bromodichloromethane Curve
y = 1137.5x + 960.97
R² = 0.9959
40000
35000
30000
25000
20000
15000
10000
5000
0
0
5
10
15
20
25
30
35


Std Dibromochloromethane Curve
y = 835.92x - 254.97
R² = 0.9999
200000
150000
100000
50000
0
-50000
0
50
100
150
200
250


Std Bromoform Curve
y = 81.075x + 503.32
R² = 0.9991
35000
30000
25000
20000
15000
10000
5000
0
0
100
200
300
400
500

APPENDIX B

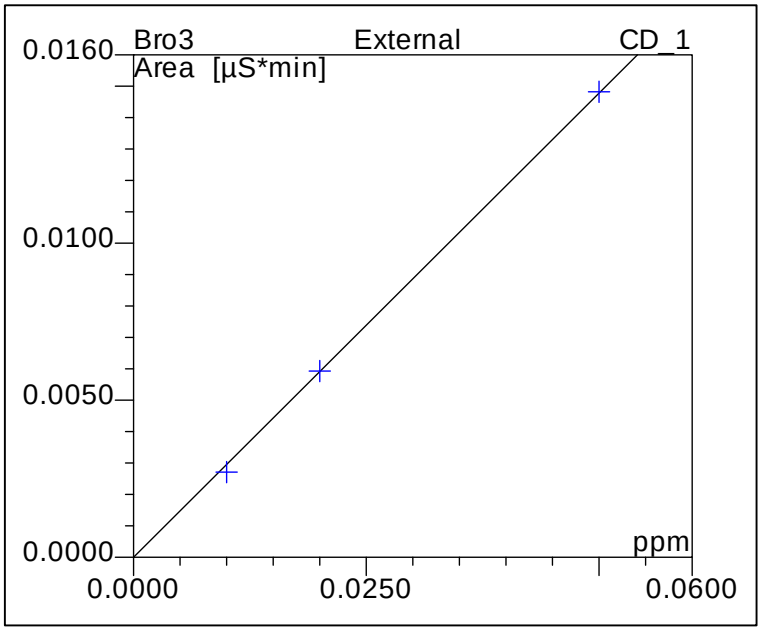
CALIBRATION CURVE OF CHLORITE



No.	Ret.Time Min	Peak Name	Cal.Type		Offset (C0)	Slope (C1)	Curve (C2)	Coeff.Det. %
5	5.02	ClO2	Lin	3	0.000	8.264	0.000	99.9835
AVERAGE:					0.0000	8.2641	0.0000	99.9835

APPENDIX C

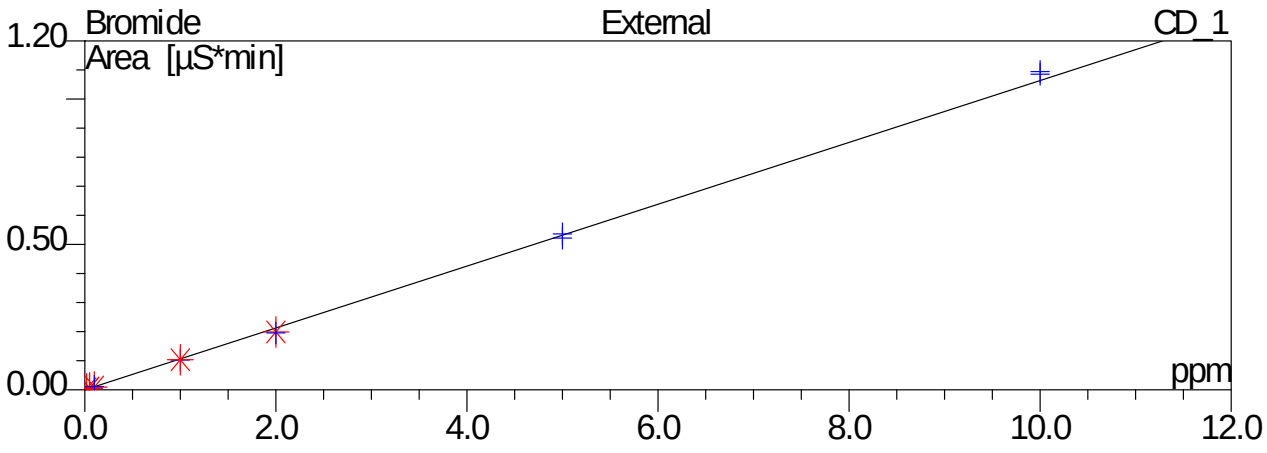
CALIBRATION CURVE OF BROMATE



Ret.Time min	Peak Name	Cal.Type	Offset (C0)	Slope (C1)	Curve (C2)	Coeff.Det. %
5.14	Bro3	Lin	0.000	0.296	0.000	99.9202
8.05	Clo3	Lin	0.000	0.456	0.000	99.2435
AVERAGE:			0.0000	0.3759	0.0000	99.5818

APPENDIX D

CALIBRATION CURVE OF BROMIDE

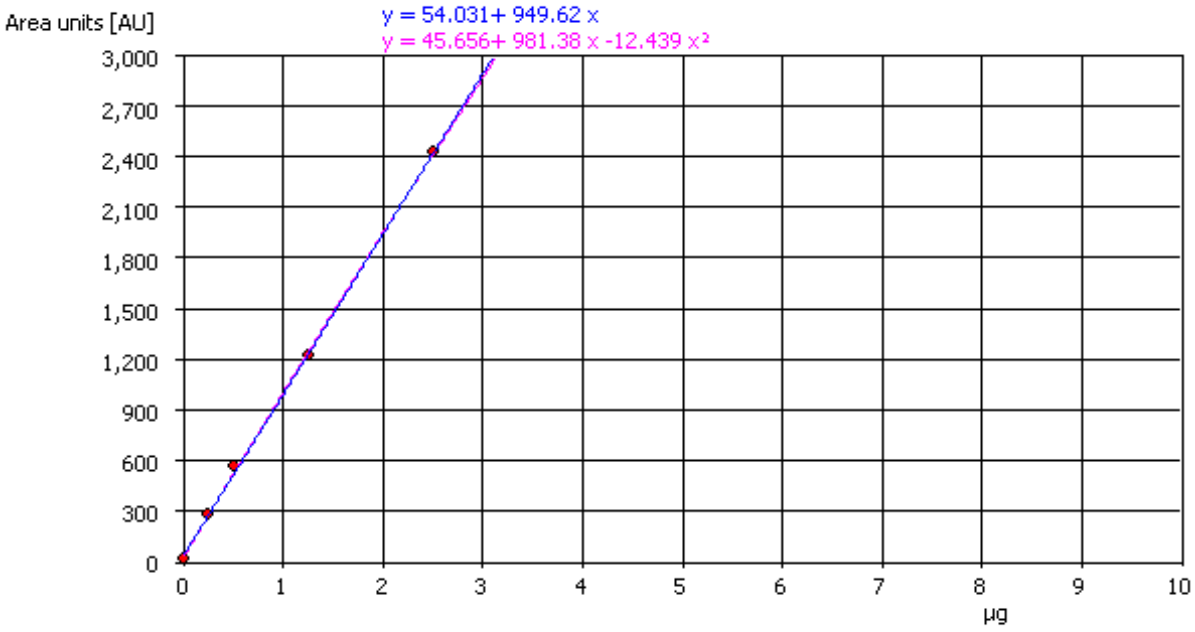

Bromide
External
CD_1
Area [µS*min]
1.20
0.50
0.00
ppm
0.0
2.0
4.0
6.0
8.0
10.0
12.0

Appendix E

CALIBRATION CURVE OF TOTAL ORGANIC CARBON

Calibration with fixed sample volume: 500.0µl

No.	Rep.	c-nom.	m-Nominal	I-Net	c-act.	c-Delta
B	Insert			1.00AU/ml		
1	1-3	0.000mg/l	0*1E-3ng	27.11AU	-0.055mg/l	
2	2-3	0.500mg/l	0.250µg	289.8AU	0.497mg/l	-0.51%
3	1-3	1.000mg/l	0.500µg	572.6AU	1.093mg/l	9.27%
4	1-3	2.500mg/l	1.25µg	1,228AU	2.472mg/l	-1.13%
5	3-3	5.000mg/l	2.50µg	2,426AU	4.993mg/l	-0.13%



APPENDIX F1

THMs DATA FOR 24 HOURS REACTION TIME

						CHCl3			CHCl2Br			CHClBr2			CHBr3				
Blending Ratio (R) (%)	**pH**	**Temp (^{o}C)**	**TOC ppm**	**TDS ppm**	**Cl_2 ppm**	**R 1**	**R 2**	**Avg**	**R 1**	**R 2**	**Avg**	**R 1**	**R 2**	**Avg**	**R 1**	**R 2**	**Avg**	**TTHMs ppb**	**Total Colifo rm**
1:2	7.1	25	0.08988	680	1.0	0.00	0.00	0.9	0.00	0.00	0.00	2.07	1.68	1.88	31.50	25.90	28.70	31.50	ND
1:2	7.0	25	0.08394	678	2.0	0.00	0.00	0.0	0.00	0.00	0.00	3.09	3.34	3.22	37.70	35.80	36.75	39.92	ND
1:2	7.0	25	0.08294	678	5.0	0.59	0.99	0.8	1.46	1.53	1.50	5.54	5.68	5.61	32.00	37.50	34.75	42.60	ND
1:2	7.1	35	0.08172	680	5.0	4.93	4.49	4.7	8.68	7.87	8.28	15.85	14.71	15.28	72.50	68.10	70.30	98.51	ND
1:2	7.0	45	0.08943	677	5.0	2.93	3.52	3.2	6.20	4.85	5.53	34.30	30.00	32.15	133.00	136.15	134.58	175.46	ND
1:5	7.0	25	0.07563	436	1.0	0.91	0.82	0.9	1.21	1.23	1.22	3.09	2.28	2.69	25.63	22.05	23.84	28.58	ND
1:5	7.0	25	0.07461	435	2.0	1.64	1.53	1.6	2.30	2.33	2.32	4.06	4.11	4.09	26.12	30.83	28.48	36.46	ND
1:5	7.0	25	0.06676	434	5.0	2.92	2.71	2.8	3.69	3.26	3.48	4.09	4.27	4.18	30.69	29.46	30.08	40.50	ND
1:5	7.0	35	0.06864	435	5.0	1.85	7.16	4.5	4.46	4.73	4.60	18.63	19.27	18.95	61.29	57.40	59.35	87.44	ND
1:5	7.0	45	0.06647	436	5.0	3.88	4.40	4.1	14.44	14.54	14.49	39.66	37.23	38.45	113.46	116.19	114.83	171.84	ND
1:10	7.0	25	0.05552	208	1.0	2.09	2.14	2.1	1.58	1.48	1.53	4.02	4.31	4.17	20.75	21.18	20.97	28.71	ND
1:10	7.0	25	0.05631	208	2.0	3.81	3.63	3.7	2.25	2.25	2.25	4.91	5.17	5.04	18.42	17.52	17.97	28.98	ND
1:10	7.0	25	0.05421	206	5.0	4.70	4.88	4.8	3.31	3.63	3.47	6.32	6.47	6.40	14.01	14.65	14.33	29.01	ND
1:10	7.0	35	0.05322	208	5.0	5.60	5.70	5.7	10.02	9.45	9.74	15.19	14.55	14.87	27.31	32.20	29.76	59.97	ND
1:10	7.0	45	0.05688	207	5.0	9.82	9.37	9.6	29.67	27.65	28.66	39.64	38.33	38.99	61.64	60.84	61.24	138.48	ND

APPENDIX F2

THMs DATA FOR 48 HOURS REACTION TIME

						$CHCl_3$			$CHCl_2Br$			$CHClBr_2$			$CHBr_3$				
Blending Ratio (R) (%)	**pH**	**Temp (^oC)**	**TOC ppm**	**TDS ppm**	**Cl_2 ppm**	**R 1**	**R 2**	**Avg**	**R 1**	**R 2**	**Avg**	**R 1**	**R 2**	**Avg**	**R 1**	**R 2**	**Avg**	**TTHMs ppb**	**Total Coliform**
1:2	7.1	25	0.08988	680	1.0	0.00	0.0	0.00	0.00	0.00	0.0	2.52	2.49	2.51	37.50	38.40	37.95	40.3	ND
1:2	7.0	25	0.08394	678	2.0	0.00	0.0	0.00	0.43	0.44	.44	4.22	3.34	3.78	46.30	44.30	45.30	49.5	ND
1:2	7.0	25	0.08294	678	5.0	1.32	2.57	1.95	6.40	6.69	6.54	13.50	12.43	12.97	40.80	39.80	40.30	61.8	ND
1:2	7.1	35	0.08172	680	5.0	0.78	1.15	.97	3.92	3.03	3.48	12.61	12.94	12.78	96.00	93.10	94.55	111.85	ND
1:2	7.0	45	0.08943	677	5.0	2.52	9.29	3.4	6.01	13.95	10.0	16.29	64.89	40.59	189.00	197.00	193.00	247	ND
1:5	7.0	25	0.07563	436	1.0	0.79	0.77	0.78	1.06	1.10	1.08	4.58	4.80	4.69	24.87	36.46	30.67	37.2	ND
1:5	7.0	25	0.07461	435	2.0	1.48	1.16	1.32	1.95	2.27	2.11	8.46	9.62	9.04	35.41	36.95	36.18	48.6	ND
1:5	7.0	25	0.06676	434	5.0	3.08	3.09	3.08	4.26	4.36	4.31	9.72	9.52	9.62	40.24	42.41	41.33	58.4	ND
1:5	7.0	35	0.06864	435	5.0	45.21	7.87	26.54	5.84	6.31	6.08	10.76	11.88	11.32	59.36	62.14	60.75	104.58	ND
1:5	7.0	45	0.06647	436	5.0	4.06	4.15	4.10	27.41	26.14	26.80	60.92	60.81	60.87	147.68	159.95	153.82	245.6	ND
1:10	7.0	25	0.05552	208	1.0	2.27	3.32	2.29	2.17	2.22	2.19	4.89	5.57	5.23	30.44	30.59	30.52	40.22	ND
1:10	7.0	25	0.05631	208	2.0	5.33	4.94	5.14	8.48	7.90	8.19	14.26	12.74	13.50	15.29	14.03	14.66	41.52	ND
1:10	7.0	25	0.05421	206	5.0	7.01	6.98	6.99	9.14	7.56	8.38	12.29	10.29	11.29	18.65	19.78	19.22	45.88	ND
1:10	7.0	35	0.05322	208	5.0	10.67	8.15	9.41	16.02	14.55	15.23	33.12	28.41	30.77	54.12	52.50	53.31	108.89	ND
1:10	7.0	45	0.05688	207	5.0	9.99	9.69	9.84	36.25	35.23	36.74	50.01	50.71	50.36	82.01	77.42	79.72	176.65	ND

ND: NOT DETECTED

APPENDIX G1

CHLORITE DATA FOR 24 HOURS REACTION TIME

						Chlorite				
Ratio	pH	Temp	TOC	TDS	ClO2	R1	R2	Avg	Time	Total Coliform
1:2	7.0	25	0.09	680.00	1	0.00	0.00	0.00	24	ND
1:2	7.0	25	0.08	678.00	2	50.00	50.00	50.00	24	ND
1:2	7.0	25	0.08	678.00	5	248.00	252.00	250.00	24	ND
1:2	7.0	35	0.08	680.00	5	264.00	256.00	260.00	24	ND
1:2	7.0	45	0.09	677.00	5	267.00	263.00	265.00	24	ND
1:5	7.0	25	0.08	436.00	1	0.00	0.00	0.00	24	ND
1:5	7.0	25	0.07	435.00	2	40.00	40.00	40.00	24	ND
1:5	7.0	25	0.07	434.00	5	261.50	258.50	260.00	24	ND
1:5	7.1	35	0.07	435.00	5	250.00	250.00	250.00	24	ND
1:5	7.1	45	0.07	436.00	5	258.00	262.00	260.00	24	ND
1:10	7.0	25	0.07	208.00	1	0.00	0.00	0.00	24	ND
1:10	7.0	25	0.07	208.00	2	0.00	0.00	0.00	24	ND
1:10	7.1	25	0.06	206.00	5	0.00	0.00	0.00	24	ND
1:10	7.0	35	0.06	208.00	5	0.00	0.00	0.00	24	ND
1:10	7.1	45	0.06	207.00	5	0.00	0.00	0.00	24	ND

APPENDIX G2

CHLORITE DATA FOR 48 HOURS REACTION TIME

						Chlorite				
Ratio	pH	Temp	TOC	TDS	ClO2	R1	R2	Avg	Time	Total Coliform
1:2	7.0	25	0.09	680.00	1	0.00	0.00	0.00	48	ND
1:2	7.0	25	0.08	678.00	2	50.00	50.00	50.00	48	ND
1:2	7.0	25	0.08	678.00	5	249.00	251.00	250.00	48	ND
1:2	7.0	35	0.08	680.00	5	266.00	254.00	260.00	48	ND
1:2	7.0	45	0.09	677.00	5	268.00	262.00	265.00	48	ND
1:5	7.0	25	0.08	436.00	1	0.00	0.00	0.00	48	ND
1:5	7.0	25	0.07	435.00	2	43.50	36.50	40.00	48	ND
1:5	7.0	25	0.07	434.00	5	260.00	260.00	260.00	48	ND
1:5	7.1	35	0.07	435.00	5	245.00	255.00	250.00	48	ND
1:5	7.1	45	0.07	436.00	5	255.20	264.80	260.00	48	ND
1:10	7.0	25	0.07	208.00	1	0.00	0.00	0.00	48	ND
1:10	7.0	25	0.07	208.00	2	0.00	0.00	0.00	48	ND
1:10	7.1	25	0.06	206.00	5	0.00	0.00	0.00	48	ND
1:10	7.0	35	0.06	208.00	5	0.00	0.00	0.00	48	ND
1:10	7.1	45	0.06	207.00	5	0.00	0.00	0.00	48	ND

APPENDIX H

BROMATE DATA FOR 5, 10 AND 20 MINUTES REACTION TIME

							Bromate (ppb)									
						Time	5 min			10 min			20 min			Total Coliform
Exp. #	pH	Temp (°C)	TOC ppm	TDS ppm	Bromide ppm	O3 Dose ppm	R1	R2	Avg	R1	R2	Avg	R1	R2	Avg	MPN
1	7.000	25	0.090	680	0.99	0.5	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	ND
2	7.010	25	0.084	678	0.98	1.0	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	ND
3	7.000	25	0.083	678	0.98	2.0	8.80	8.80	8.80	9.00	9.50	9.25	10.70	10.30	10.50	ND
4	6.990	15	0.082	680	0.98	2.0	7.70	7.70	7.70	8.20	8.60	8.40	9.80	9.90	9.85	ND
5	6.990	45	0.090	677	0.99	2.0	116.50	114.60	115.55	121.50	121.50	121.50	153.00	152.93	152.97	ND
6	7.000	25	0.085	678	0.98	5.0	261.00	258.50	259.75	268.60	268.60	268.60	308.70	306.00	307.35	ND
7	6.990	25	0.075	436	0.45	0.5	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	ND
8	7.000	25	0.075	435	0.44	1.0	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	ND
9	7.010	25	0.067	434	0.46	2.0	0.00	0.00	0.00	8.60	8.60	8.60	9.50	10.50	10.00	ND
10	6.980	15	0.069	435	0.45	2.0	8.40	8.60	8.50	0.00	0.00	0.00	0.00	0.00	0.00	ND
11	6.990	45	0.066	436	0.45	2.0	0.00	0.00	0.00	68.90	67.00	67.95	76.00	76.00	76.00	ND
12	6.990	25	0.067	435	0.45	5.0	46.80	44.00	45.40	229.00	228.60	228.80	250.00	247.80	248.90	ND
13	7.000	25	0.066	208	0.22	0.5	220.00	220.30	220.15	0.00	0.00	0.00	0.00	0.00	0.00	ND
14	7.020	25	0.066	208	0.21	1.0	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	ND
15	6.990	25	0.064	206	0.23	2.0	0.00	0.00	0.00	7.90	7.80	7.85	9.00	9.00	9.00	ND
16	7.000	15	0.063	208	0.21	2.0	4.70	4.70	4.70	0.00	0.00	0.00	0.00	0.00	0.00	ND
17	7.000	45	0.060	207	0.22	2.0	18.09	18.01	18.05	23.65	23.65	23.65	29.07	29.03	29.05	ND
18	7.000	25	0.061	206	0.22	5.0	185.75	186.60	185.20	207.20	208.50	207.85	235.80	234.80	235.30	ND

VITA

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